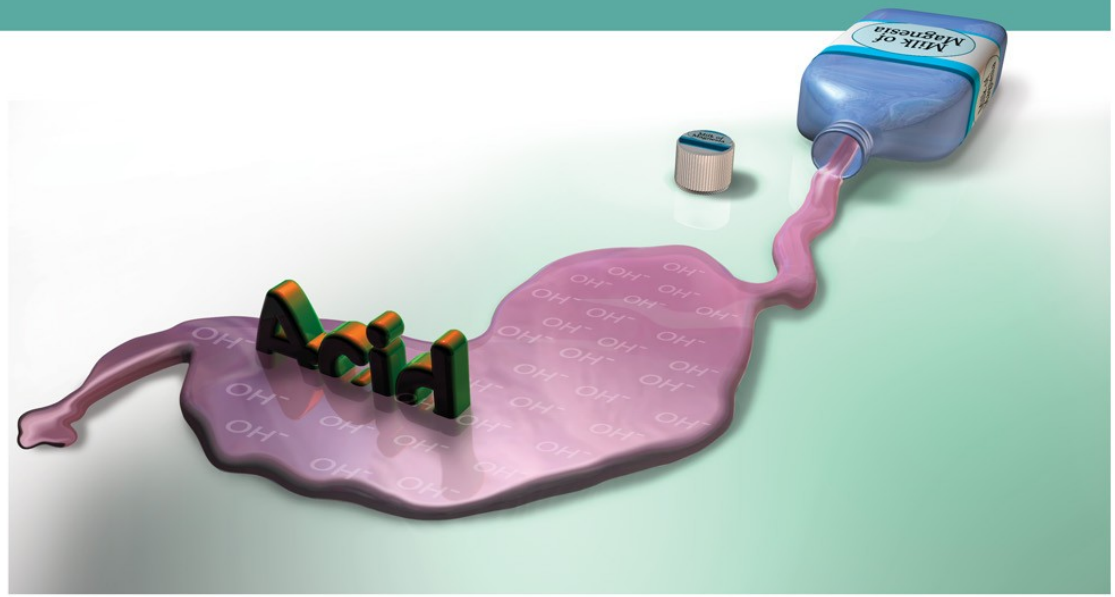
John E. McMurray – Robert C. Fay

GENERAL CHEMISTRY: ATOMS FIRST

Chapter 14 Acids and Bases



Prentice Hall

Properties of Acids

- sour taste
- react with “active” metals
  - ✓ i.e., Al, Zn, Fe, but not Cu, Ag, or Au

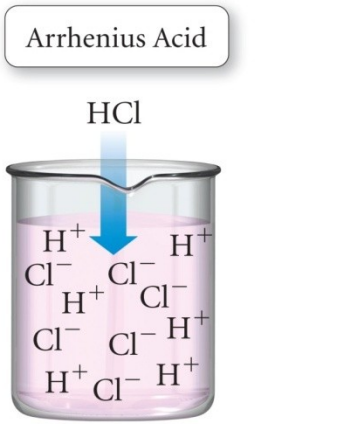
    $2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2$
  - ✓ corrosive
- react with carbonates, producing CO_2
  - ✓ marble, baking soda, chalk, limestone

    $CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O$
- acid changes the color of vegetable dyes
  - ✓ blue litmus turns red
- react with bases to form ionic salts

Properties of Bases

- also known as alkalis
- taste bitter
  - ✓ alkaloids = plant product that is alkaline
    - ➢ often poisonous
- solutions feel slippery
- change color of vegetable dyes
  - ✓ different color than acid
  - ✓ red litmus turns blue
- react with acids to form ionic salts
  - ✓ **neutralization**

Acid-Base Concepts: The ARRHENIUS Theory



$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

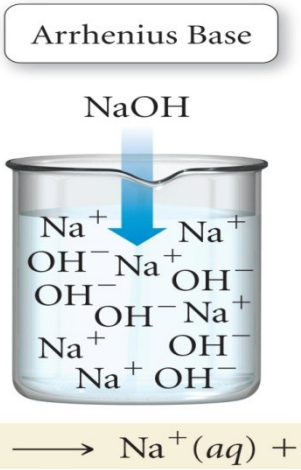
HCl ionizes in water, producing H^+ and Cl^- ions

Arrhenius Acid: A substance that dissociates in water to produce hydrogen ions, H^{1+}.

$$HA(aq) \rightleftharpoons H^{1+}(aq) + A^{1-}(aq)$$

Arrhenius Base: A substance that dissociates in water to produce hydroxide ions, OH^{1-}.

$$MOH(aq) \rightleftharpoons M^{1+}(aq) + OH^{1-}(aq)$$



$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

NaOH dissociates in water, producing Na^+ and OH^- ions

Arrhenius Acid-Base Reactions

- the H^+ from the acid combines with the OH^- from the base to make a molecule of H_2O
  - ✓it is often helpful to think of H_2O as H-OH
- the cation from the base combines with the anion from the acid to make a salt

acid + base → salt + water

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Arrhenius Theory Doesn't Explain

- ✓ why molecular substances, like NH_3, dissolve in water to form basic solutions – even though they do not contain OH^- ions
- ✓ does not explain how some ionic compounds, like Na_2CO_3 or Na_2O, dissolve in water to form basic solutions – even though they do not contain OH^- ions
- ✓ why molecular substances, like CO_2, dissolve in water to form acidic solutions – even though they do not contain H^+ ions
- ✓ acid-base reactions that take place outside aqueous solution

Acid-Base Concepts: The Brønsted-Lowry Theory

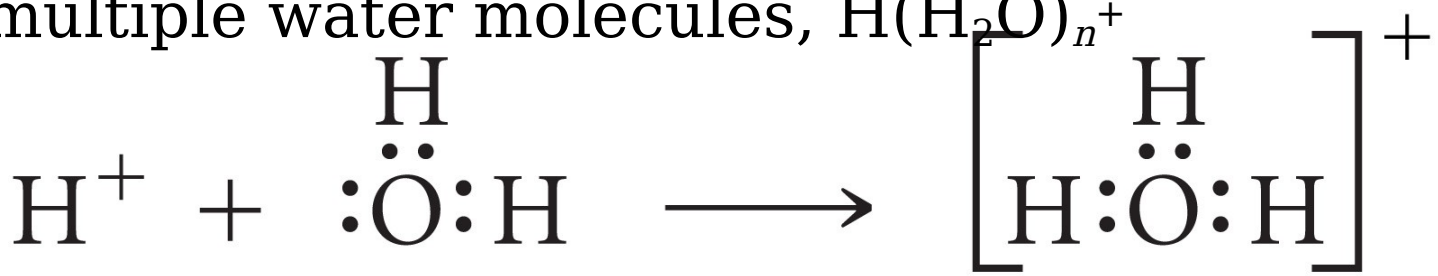
- **Brønsted-Lowry Acid**: A substance that can transfer (donate) hydrogen ions, H^+ (a proton donor).
- **Brønsted-Lowry Base**: A substance that can accept hydrogen ions, H^+ (a proton acceptor).
- broader definition than Arrhenius
- does not have to take place in aqueous solution
- one of the advantages of Brønsted-Lowry theory is that it allows reactions to be

Hydronium Ion

- the H^+ ions produced by the acid are so reactive they cannot exist in water
  - ✓ H^+ ions are protons!!
- instead, they react with a water molecule(s) to produce complex ions, mainly **hydronium ion, H_3O^+**

$$H^+ + H_2O \rightarrow H_3O^+$$

  - ✓ there are also minor amounts of H^+ with multiple water molecules, $H(H_2O)_n^+$



Amphoteric Substances

- **amphoteric substances** can act as either an acid or a base
  - ✓ have both transferable H^+ and lone pair electrons
- water acts as base, accepting H^+ from HCl

$$HCl(aq) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$

- water acts as acid, donating H^+ to NH_3

$$NH_3(aq) + H_2O(l) \Leftrightarrow NH_4^+(aq) + OH^-(aq)$$

Conjugate Pairs

- In a Brønsted-Lowry Acid-Base reaction,
  - ✓ the original base gains a proton and becomes an acid in the reverse reaction, and
  - ✓ the original acid loses a proton and becomes a base in the reverse process

$$H\text{–}A + :B \Leftrightarrow :A^{-} + H\text{–}B^{+}$$

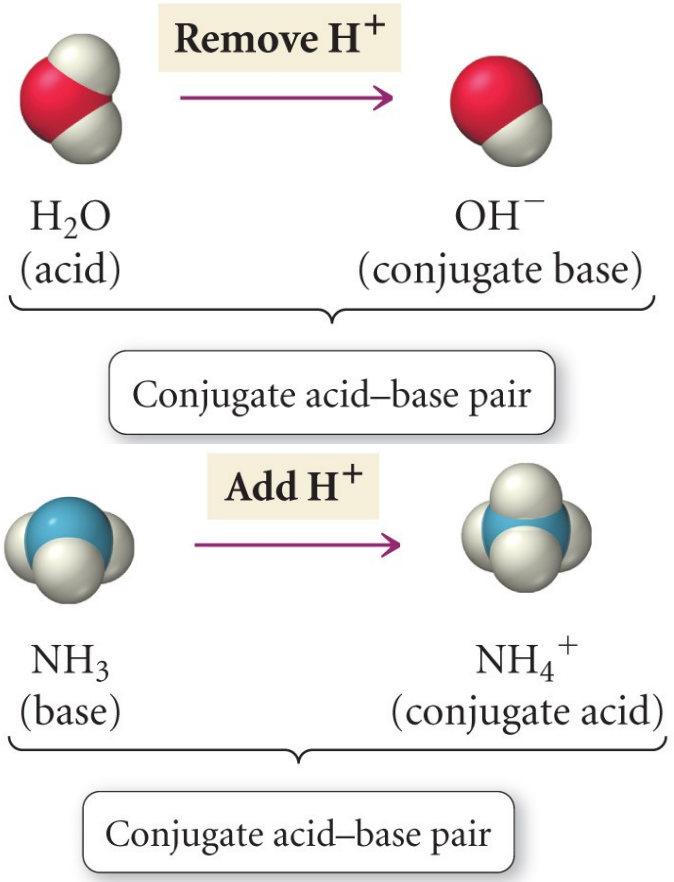
- each acid and the base it becomes AND each base and the acid it becomes
  - ✓ are called a **conjugate pair**
  - ✓ the original base becomes the conjugate acid; and the original acid becomes the conjugate base

Conjugate Pairs

In the reaction $H_2O + NH_3 \Leftrightarrow HO^- + NH_4^+$

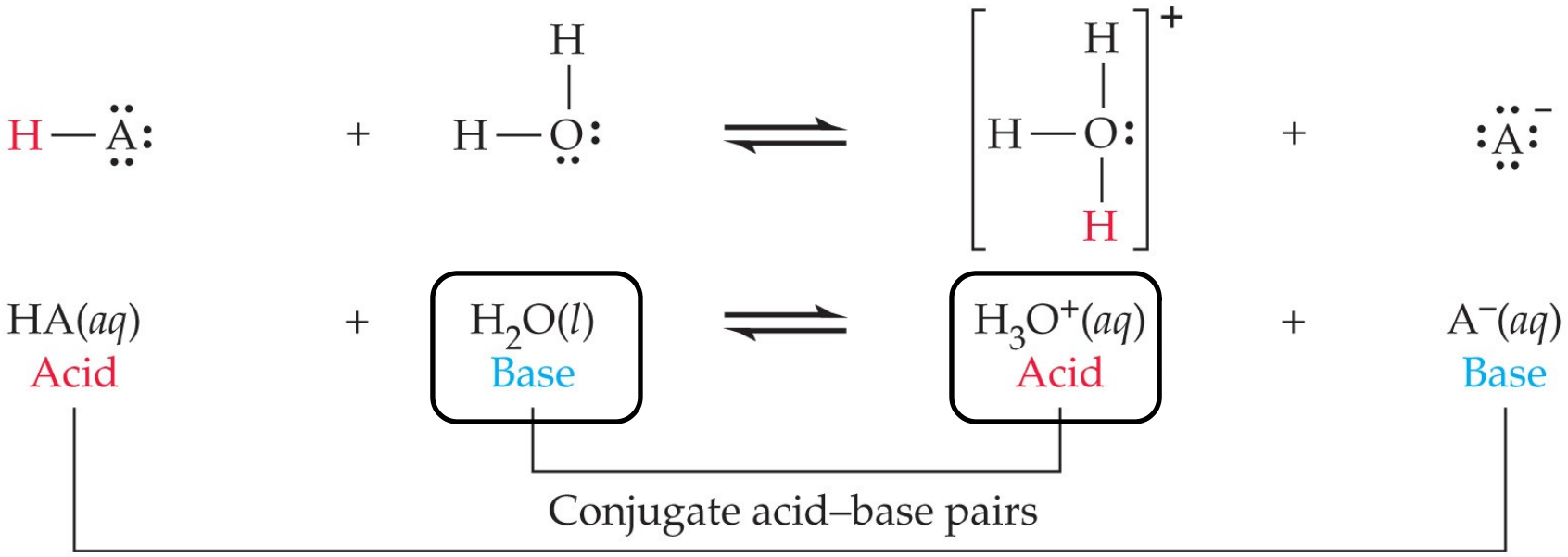
H_2O and HO^- constitute an Acid/Conjugate Base pair

NH_3 and NH_4^+ constitute a Base/Conjugate Acid pair



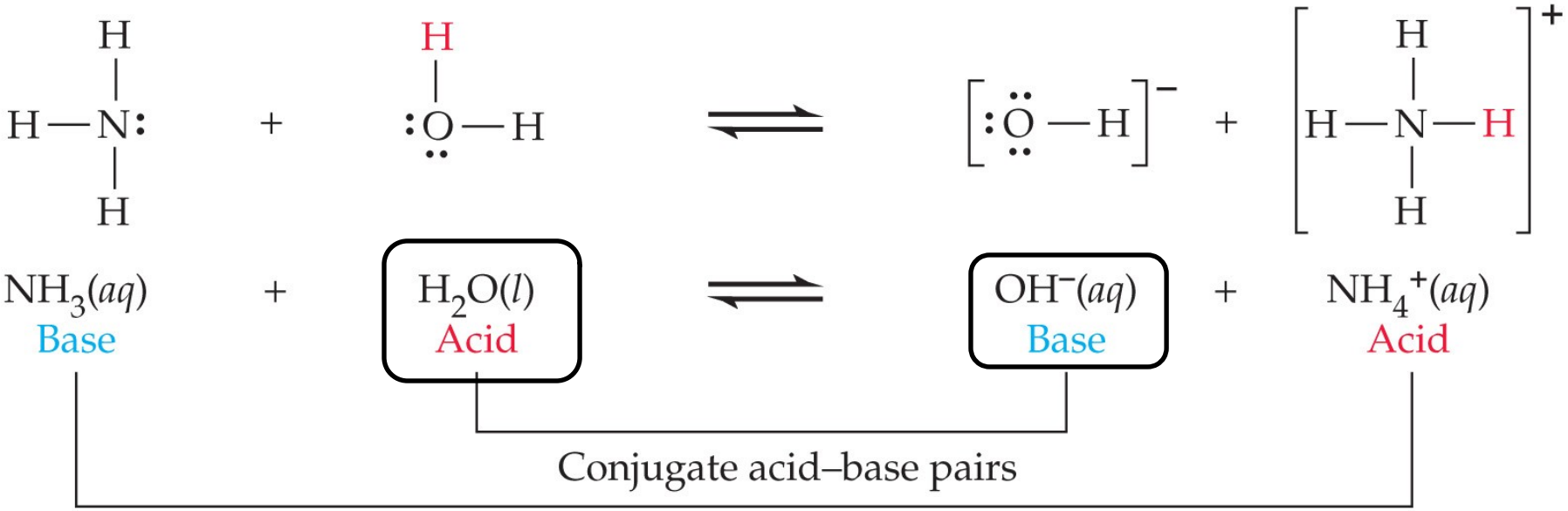
Acid-Base Concepts: The Brønsted-Lowry Theory

Acid-Dissociation Equilibrium – Conjugate acids and bases



Acid-Base Concepts: The Brønsted-Lowry Theory

Base-Dissociation Equilibrium – Conjugate bases and acids

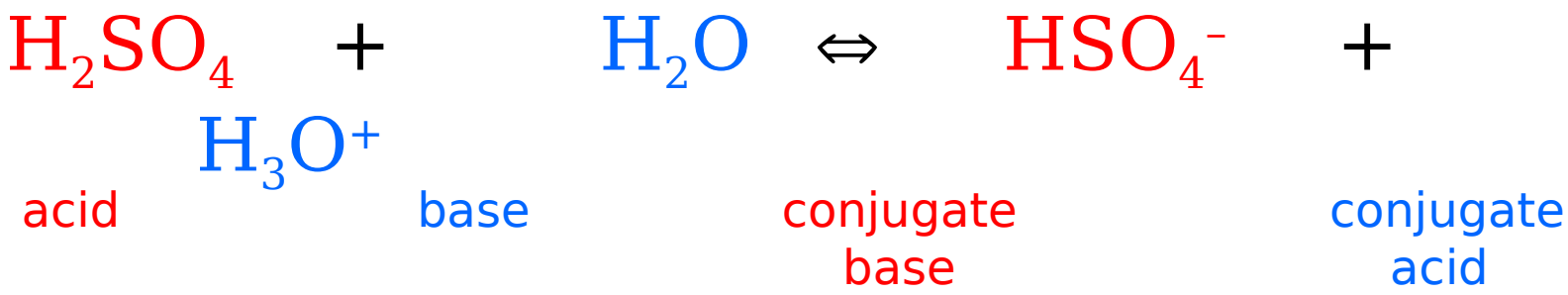


Brønsted-Lowry Acid-Base Reactions

$HCHO_2$ + H_2O ⇔ CHO_2^- + H_3O^+

acid base conjugate base conjugate acid

Identify the Brønsted-Lowry Acids and Bases and Their Conjugates in the Reaction



When the H_2SO_4 becomes HSO_4^-, it lost an H^+ - so H_2SO_4 must be the acid and HSO_4^- its conjugate base

When the H_2O becomes H_3O^+, it accepted an H^+ - so H_2O must be the base and H_3O^+ its conjugate acid

Identify the Brønsted-Lowry Acids and Bases and Their Conjugates in the Reaction

HCO_3^- + H_2O ⇔ H_2CO_3 + HO^-

When the HCO_3^- becomes H_2CO_3, it accepted an H^+ - so HCO_3^- must be the base and H_2CO_3 its conjugate acid

When the H_2O becomes OH^-, it donated an H^+ - so H_2O must be the acid and OH^- its conjugate base

HCO_3^- + H_2O ⇔ H_2CO_3 + HO^-

base — acid — conjugate acid — conjugate base

Write the formula for the conjugate acid of the following

H_2O

NH_3

CO_3^{2-}

$H_2PO_4^{1-}$

Write the formula for the conjugate acid of the following

H_2O H_3O^+

NH_3 NH_4^+

CO_3^{2-} HCO_3^-

$H_2PO_4^{1-}$ H_3PO_4

Write the formula for the conjugate base of the following

H_2O

NH_3

CO_3^{2-}

$H_2PO_4^{1-}$

Write the formula for the conjugate base of the following

H_2O HO^-

NH_3 NH_2^-

CO_3^{2-} since CO_3^{2-} does not have an H, it cannot be an acid

$H_2PO_4^{1-}$ HPO_4^{2-}

Polyprotic Acids

- often acid molecules have more than one ionizable hydrogen – these are called **polyprotic acids**

the ionizable H's may have different acid strengths or be equal

1 H = Monoprotic, Example: HCl

2 H = Diprotic, Example: H_2SO_4

3 H = Triprotic, Example: H_3PO_4

Polyprotic Acids

- polyprotic acids ionize in steps
  - ✓each ionizable H (proton) is removed sequentially

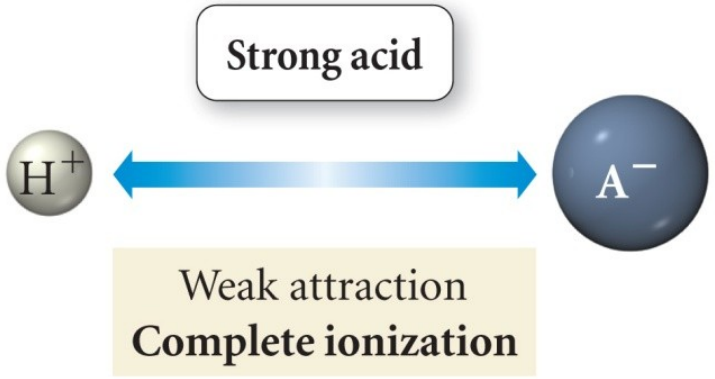
- removing of the 1st H automatically makes removal of the 2nd H harder
  - ✓H_2SO_4 is a stronger acid than HSO_4^-

Strong or Weak

- a strong acid is a strong electrolyte
  - practically all the acid molecules ionize, $\longrightarrow$
- a strong base is a strong electrolyte
  - practically all the base molecules form OH^- ions, either through dissociation or reaction with water, $\longrightarrow$
- a weak acid is a weak electrolyte
  - only a small percentage of the molecules ionize, $\Leftrightarrow$
- a weak base is a weak electrolyte
  - only a small percentage of the base molecules form OH^- ions, either through dissociation or reaction with water, $\Leftrightarrow$

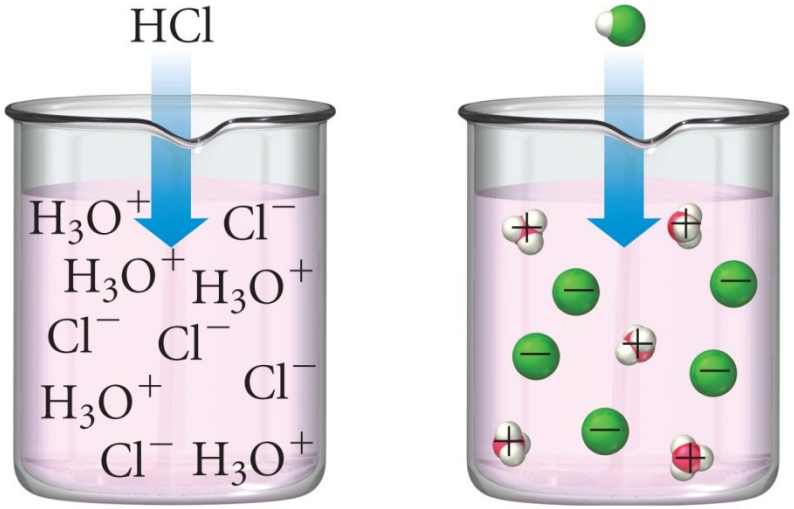
Strong Acids

- The stronger the acid, the more willing it is to donate H
  - ✓ use water as the standard base
- strong acids donate practically all their H's to water
  - ✓ 100% ionized in water
  - ✓ strong electrolyte
- $[H_3O^+] = [\text{strong acid}]$



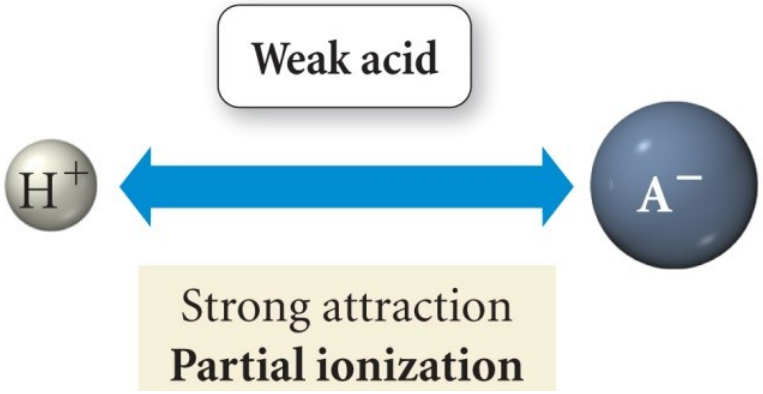
$HCl \rightarrow H^+ + Cl^-$

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$



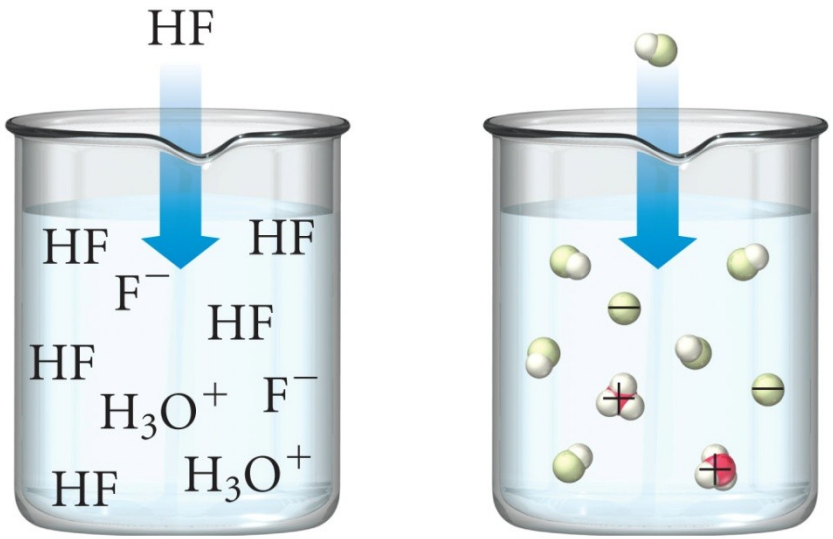
Weak Acids

- weak acids donate a small fraction of their H's
  - ✓most of the weak acid molecules do not donate H to water
  - ✓much less than 1% ionized in water
- $[H_3O^+] << [\text{weak acid}]$
- $[H_3O^+] << [HF]$



$$HF \Leftrightarrow H^+ + F^-$$

$$HF + H_2O \Leftrightarrow H_3O^+ + F^-$$



Increasing Acidity

Acids	Conjugate Bases
$HClO_4$	ClO_4^{-1}
H_2SO_4	HSO_4^{-1}
HI	I^{-1}
HBr	Br^{-1}
HCl	Cl^{-1}
HNO_3	NO_3^{-1}
H_3O^{+1}	H_2O
HSO_4^{-1}	SO_4^{-2}
H_2SO_3	HSO_3^{-1}
H_3PO_4	$H_2PO_4^{-1}$
HNO_2	NO_2^{-1}
HF	F^{-1}
$HC_2H_3O_2$	$C_2H_3O_2^{-1}$
H_2CO_3	HCO_3^{-1}
H_2S	HS^{-1}
NH_4^{+1}	NH_3
HCN	CN^{-1}
HCO_3^{-1}	CO_3^{-2}
HS^{-1}	S^{-2}
H_2O	OH^{-1}
$CH_3\text{-}C(O)\text{-}CH_3$	$CH_3\text{-}C(O)\text{-}CH_2^{-1}$
NH_3	NH_2^{-1}
CH_4	CH_3^{-1}
OH^{-1}	O^{-2}

Increasing Basicity

Strengths of Acids & Bases

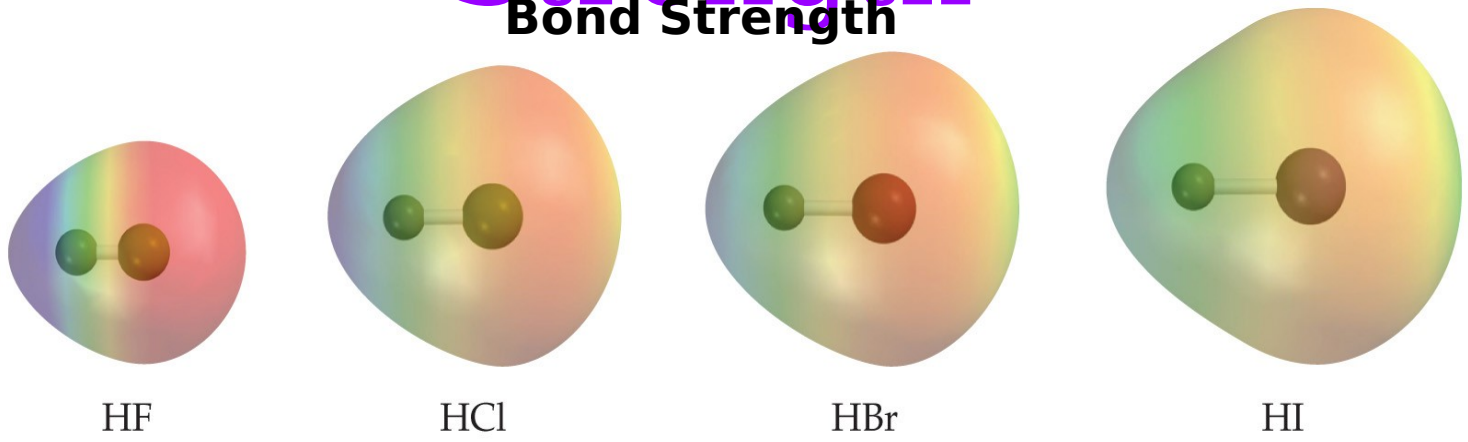
- commonly, acid or base strength is measured by determining the equilibrium constant of a substance's reaction with water

$$HA + H_2O \Leftrightarrow A^- + H_3O^+$$
$$B: + H_2O \Leftrightarrow HB^+ + OH^-$$

- the farther the equilibrium position lies to the products, the stronger the acid or base
- the position of equilibrium depends on the strength of attraction between the base form and the H^+
  - ✓ stronger attraction means stronger base or weaker acid

Factors That Affect Acid Strength

Bond Strength



Acid strength

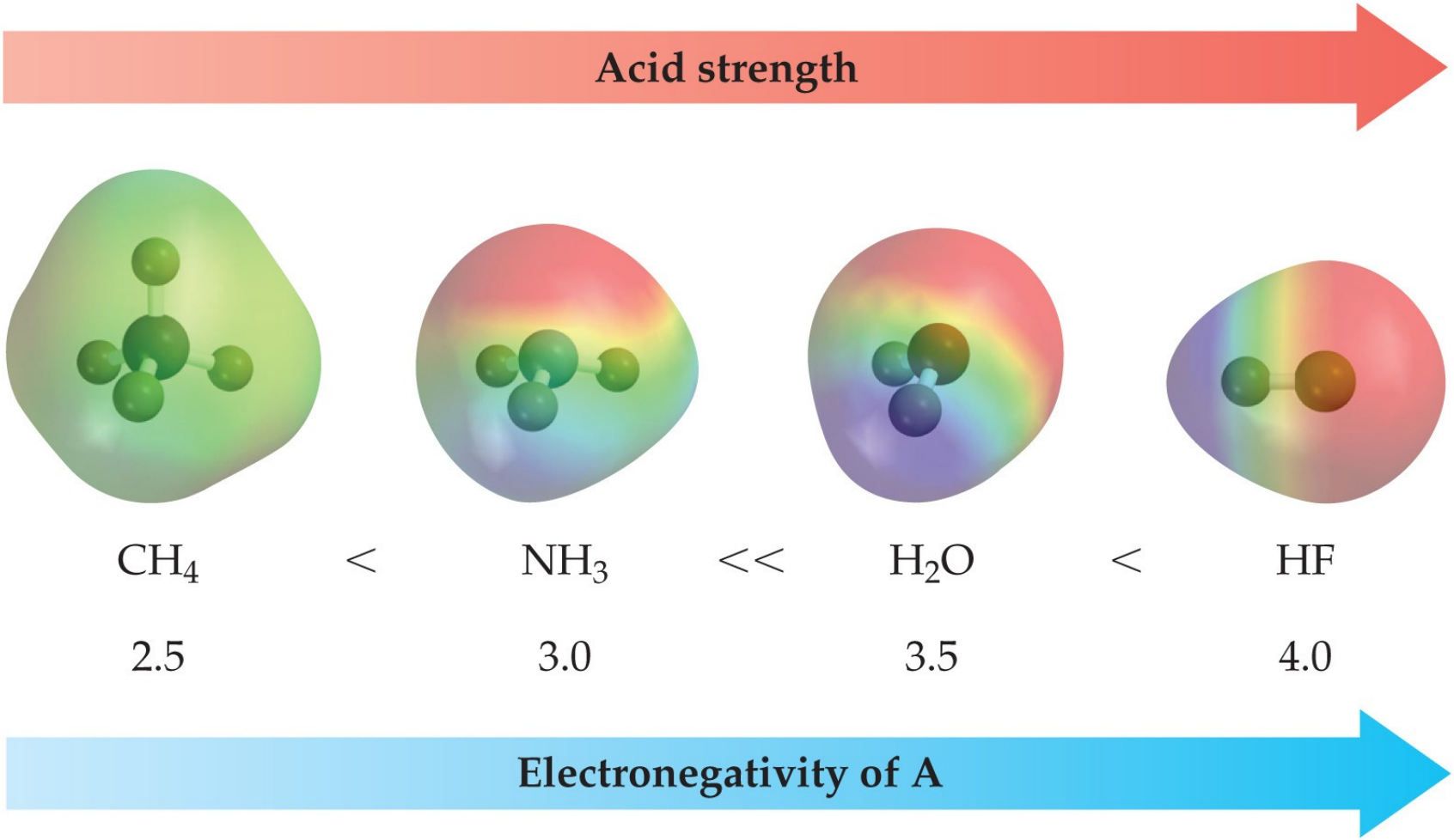
HF << HCl < HBr < HI

570 431 366 298

H–A bond strength (kJ/mol)

Factors That Affect Acid Strength

Bond Polarity



Factors That Affect Acid Strength

Oxoacids

Acid strength

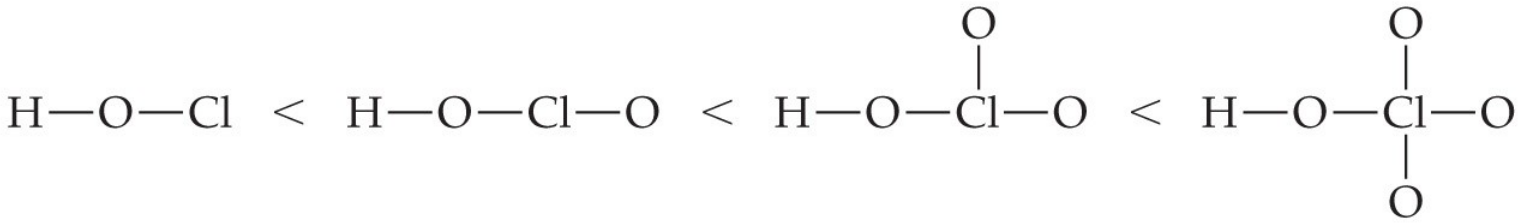
	H–O–I	<	H–O–Br	<	H–O–Cl
Dissociation constant, K_a	2.3×10^{-11}		2.0×10^{-9}		3.5×10^{-8}
Electronegativity	2.5		2.8		3.0

Electronegativity of Y

Factors That Affect Acid Strength

Oxoacids

Acid strength; number of O atoms



Name of acid	Hypochlorous	Chlorous	Chloric	Perchloric
Dissociation constant, K_a	3.5×10^{-8}	1.2×10^{-2}	~1	Very large
Oxidation number of Cl	+1	+3	+5	+7

Oxidation number of Cl

in HOCl the H is +1, the O is -2, and Cl is +1

in HOClO the OH is -1, the O is -2, and the Cl is +3

in HOClOO the OH is -1, both O are -2 each, and the Cl is +5

in HOClOOO the OH is -1, all 3 O are -2 each, and the Cl is +7

General Trends in Acidity

- **the stronger an acid is at donating H, the weaker the conjugate base is at accepting H**
- higher oxidation number = stronger oxyacid
  - ✓ $H_2SO_4 > H_2SO_3$
  - ✓ $HNO_3 > HNO_2$
- a cation is a stronger acid than a neutral molecule; a neutral molecule is a stronger acid than an anion
  - ✓ $H_3O^+ > H_2O > OH^-$
  - ✓ $NH_4^+ > NH_3 > NH_2^-$
  - ✓ base trend opposite

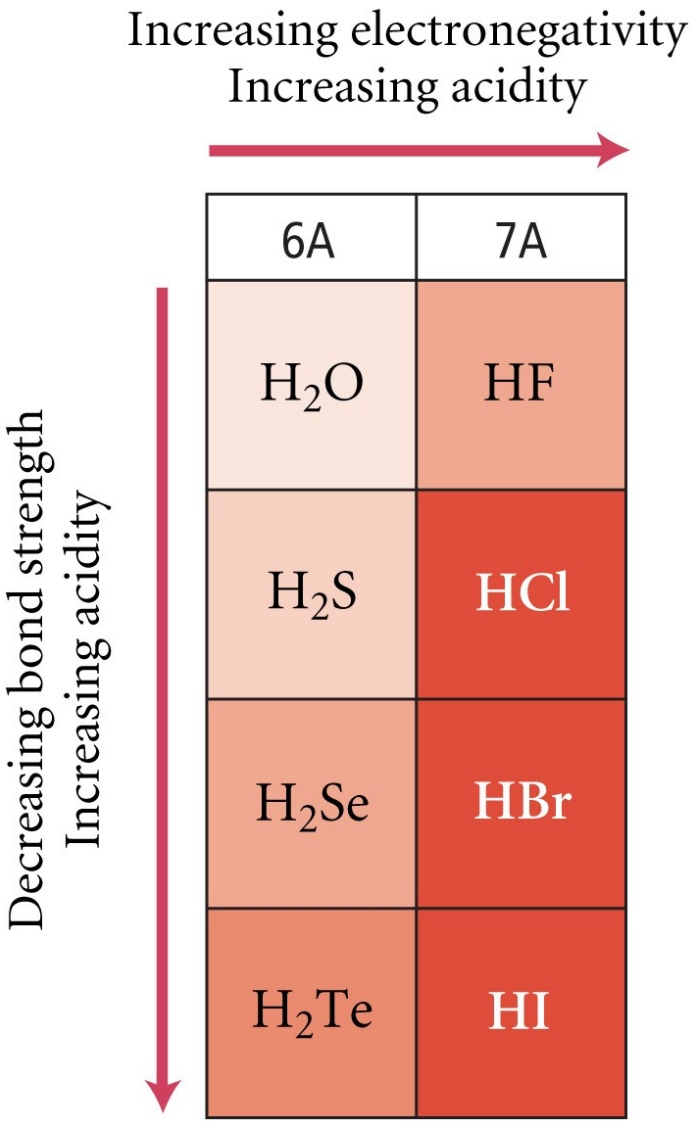
Strengths of Binary Acids

- the more polarized the bond, the more acidic the bond

  δ+ δ-

  H-X

- the stronger the H-X bond, the weaker the acid
- binary acid strength increases to the right across a period
  - ✓ H-C < H-N < H-O < H-F
- binary acid strength increases down the column
  - ✓ H-F < H-Cl < H-Br < H-I



Acid Ionization Constant, K_a

- acid strength measured by the size of the equilibrium constant when react with H_2O

$$HAcid + H_2O \Leftrightarrow Acid^- + H_3O^+$$

- the equilibrium constant is called the **acid ionization constant, K_a**
  - ✓larger K_a = stronger acid

$$K_a = \frac{[Acid] \times [H_3O^+]}{[HAcid]}$$

Relation Between K_a and K_b

$$NH_4^{1+}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + NH_3(aq) \qquad K_a$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^{1+}(aq) + OH^{1-}(aq) \qquad K_b$$

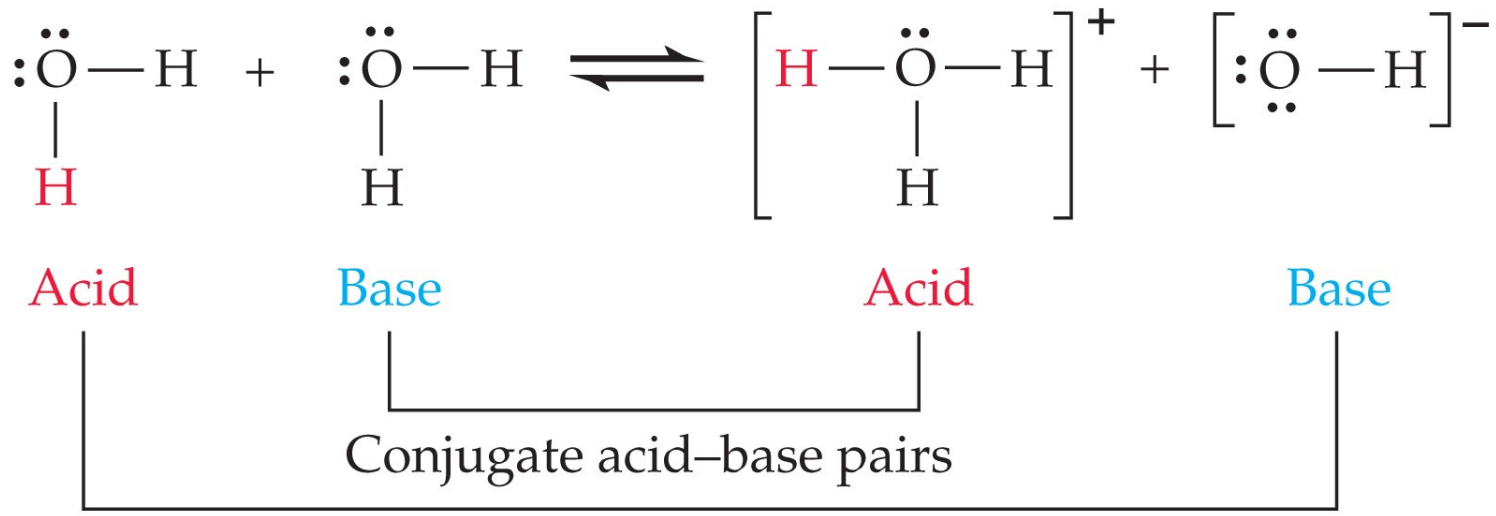
$$2H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + OH^{1-}(aq) \qquad K_w$$

$$K_a \times K_b = \frac{[H_3O^{1+}][NH_3]}{[NH_4^{1+}]} \times \frac{[NH_4^{1+}][OH^{1-}]}{[NH_3]} = [H_3O^{1+}][OH^{1-}] = K_w$$

Auto-ionization of Water

- Water is actually an extremely weak electrolyte
- about 1 out of every 10 million water molecules form ions through a process called **auto-ionization**
- all aqueous solutions contain **both** H_3O^+ and OH^-
  - ✓ the concentration of H_3O^+ and OH^- are equal in water
- as $[H_3O^+]$ increases the $[OH^-]$ must decrease so the product stays constant

Dissociation of Water



Dissociation of Water: $2H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + OH^{1-}(aq)$

Ion-Product Constant for Water: $K_w = [H_3O^{1+}][OH^{1-}]$

at 25°C: $[H_3O^{1+}] = [OH^{1-}] = 1.0 \times 10^{-7}$ M

$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = \mathbf{1.0 \times 10^{-14}}$

Dissociation of Water

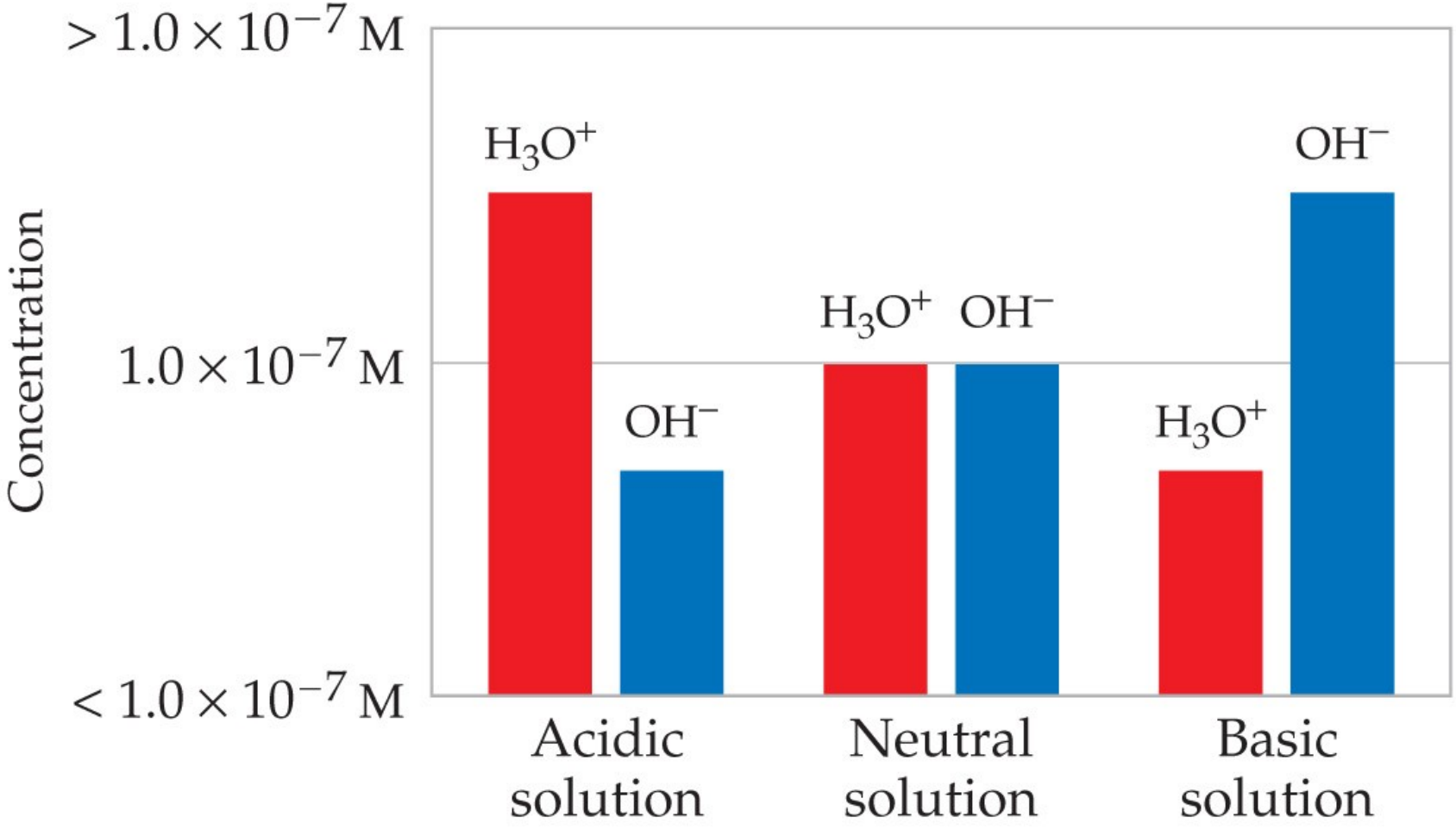
- the product of the H_3O^+ and OH^- concentrations is always the same number
- the number is called the **ion product** of water and has the symbol K_w

$$K_w = [H_3O^{1+}][OH^{1-}] = 1.0 \times 10^{-14}$$

$$[H_3O^{1+}] = \frac{K_w}{[OH^{1-}]} = \frac{1.0 \times 10^{-14}}{[OH^{1-}]}$$

$$[OH^{1-}] = \frac{K_w}{[H_3O^{1+}]} = \frac{1.0 \times 10^{-14}}{[H_3O^{1+}]}$$

Dissociation of Water



Calculate the $[OH^-]$ at 25°C when the $[H_3O^+]$ = 1.5 x 10^{-9} M, and determine if the solution is acidic, basic, or neutral

Given: $[H_3O^+] = 1.5 \times 10^{-9}$ M

Find: $[OH^-]$

Concept Plan: $[H_3O^+] \rightarrow [OH^-]$

$$K_w = [H_3O^+][OH^-]$$

Relationships:

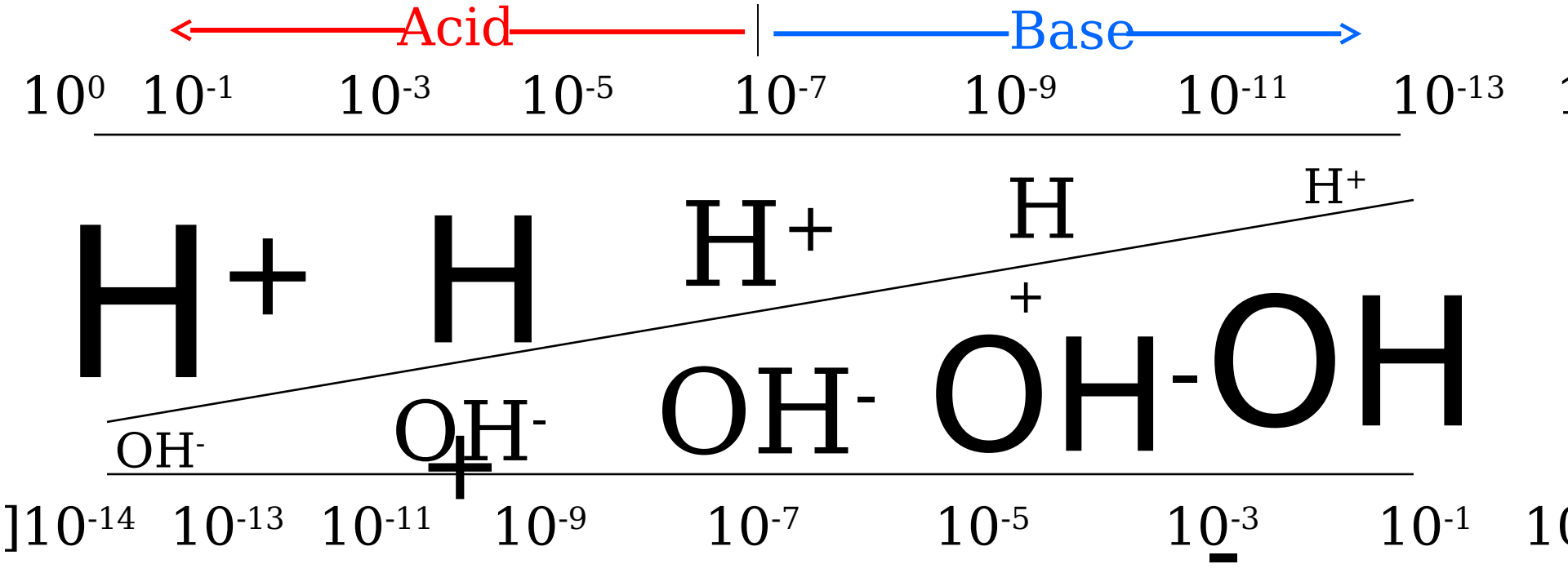
$$K_w = [H_3O^+][OH^-]$$

Solution:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6}\ \text{M} \qquad [OH^-] = \frac{K_w}{[H_3O^+]}$$

Check: The units are correct. The fact that the $[H_3O^+] < [OH^-]$ means the solution is basic

Complete the Table
$[H^+]$ vs. $[OH^-]$



en though it may look like it, neither H^+ nor OH^- will ever b

the sizes of the H^+ and OH^- are not to scale

because the divisions are powers of 10 rather than units

stop

pH

- solution acidity/basicity is often expressed as **pH**
- $pH = -\log[H_3O^+]$
- $[H_3O^+] = 10^{-pH}$
  - pH < 7 is acidic
  - pH > 7 is basic
  - pH = 7 is neutral
    - $pH_{water} = -\log[10^{-7}] = 7$

Sig. Figs. & Logs

- For the log of a number written in scientific notation:

$$\log(2.0 \times 10^6) = \log(10^6) + \log(2.0) = 6 + 0.30303...$$

$$= \quad 6.30303...$$

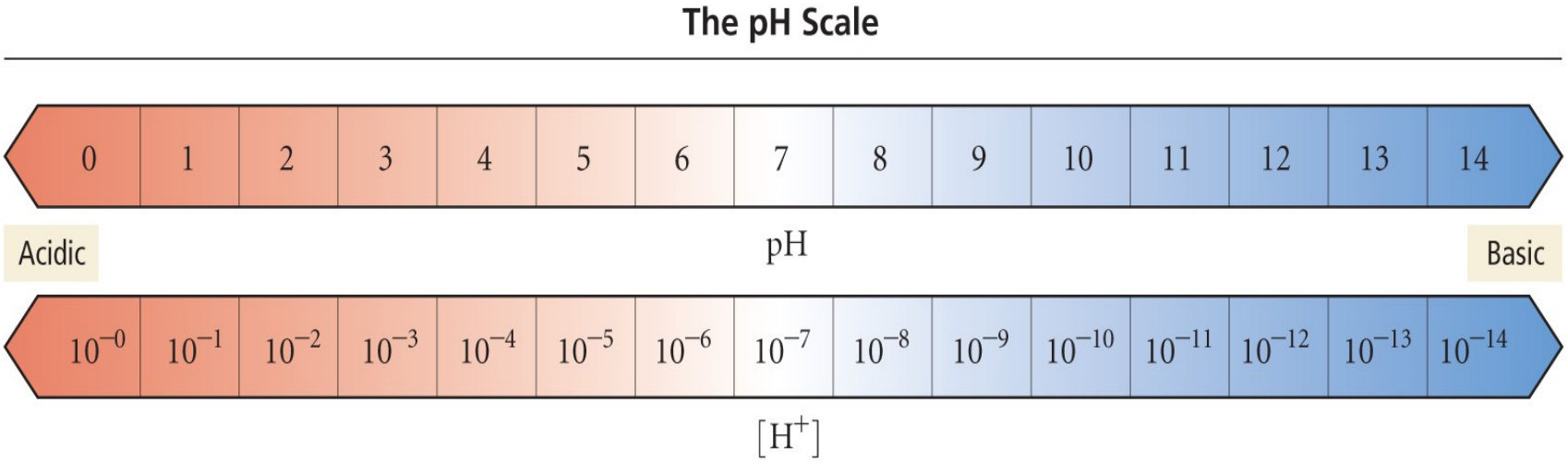
  - ✓ the digit(s) before the decimal point come from the exponent on 10,
  - ✓ the digits after the decimal point come from the decimal part of the number

- the decimal part of the scientific notation number determines the significant figures, **the sig figs are the digits after the decimal point in the log**

$$\log(2.0 \times 10^6) = 6.30$$

pH

- the lower the pH, the more acidic the solution; the higher the pH, the more basic the solution
  - ✓1 pH unit corresponds to a factor of 10 difference in acidity
- normal range 0 to 14
  - ✓pH 0 is $[H^+] = 1$ M, pH 14 is $[OH^-] = 1$ M
  - ✓pH can be negative (very acidic) or larger



pH of Common Substances

Substance	pH
1.0 M HCl	0.0
0.1 M HCl	1.0
stomach acid	1.0 to 3.0
lemons	2.2 to 2.4
soft drinks	2.0 to 4.0
plums	2.8 to 3.0
apples	2.9 to 3.3
cherries	3.2 to 4.0
unpolluted rainwater	5.6
human blood	7.3 to 7.4
egg whites	7.6 to 8.0
milk of magnesia (sat'd $Mg(OH)_2$)	10.5
household ammonia	10.5 to 11.5
1.0 M NaOH	14

Calculate the pH at 25°C when the $[OH^-]$ = 1.3×10^{-2} M, and determine if the solution is acidic, basic, or neutral

Given:	$[OH^-] = 1.3 \times 10^{-2}$ M
Find:	pH
Concept Plan:	$[OH^-] \rightarrow [H_3O^+] \rightarrow pH$
Relationships:	$K_w = [H_3O^+][OH^-]$ $\quad pH = -\log[H_3O^+]$
Solution:	$K_w = [H_3O^+][OH^-]$ $\quad [H_3O^+] = 7.7 \times 10^{-13}$ M $[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-2}}$ $\quad pH = -\log(7.7 \times 10^{-13})$ $pH = 12.11$
Check:	pH is unitless. The fact that the pH > 7 means the solution is basic

pOH

- acidity/basicity can also be expressed as **pOH**
  - $pOH = -\log[OH^-]$
  - $[OH^-] = 10^{-pOH}$
    - $pOH_{water} = -\log[10^{-7}] = 7$
- pOH < 7 is basic
- pOH > 7 is acidic

pH

pOH

Relationship between pH and pOH

- **the sum of the pH and pOH of a solution = 14.00**
  - ✓at 25°C
  - ✓can use pOH to find pH of a solution

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$\left(-\log[H_3O^+][OH^-]\right) = -\log 1.0 \times 10^{-14}$$

$$\left(-\log[H_3O^+]\right) + \left(-\log[OH^-]\right) = 14.00$$

$$pH + pOH = 14.00$$

pK

- a way of expressing the strength of an acid or base is **pK**
  - pK_a = -log(K_a),
  - $K_a = 10^{-pKa}$
  - pK_b = -log(K_b),
  - $K_b = 10^{-pKb}$
- **the stronger the acid, the smaller the pK_a**
  - larger K_a = smaller pK_a
    - because it is the –log
    - – log 5 = –0.7 but the –log 1250 = – 3.1 (more negative, hence smaller number)

The pH in Solutions of Strong Acids

What is the pH of a 0.025 M solution of HNO_3?

$$HNO_3(aq) + H_2O(l) \xrightarrow{100\%} H_3O^{1+}(aq) + NO_3^{1-}(aq)$$

Since HNO_3 is a strong acid, $[H_3O^{1+}] = [HNO_3]$.

$$pH = -\log([H_3O^{1+}]) = -\log(0.025) = 1.60$$

The pH in Solutions of Strong Bases

What is the pH of a 0.025 M solution of NaOH?

$$NaOH(aq) \xrightarrow{100\%} Na^{1+}(aq) + OH^{1-}(aq)$$

Since NaOH is a strong base, $[OH^{1-}] = [NaOH]$.

$$[H_3O^{1+}] = \frac{1.0 \times 10^{-14}}{[OH^{1-}]} = \frac{1.0 \times 10^{-14}}{0.025} = 4.0 \times 10^{-13}\ M$$

$$pH = -\log([H_3O^{1+}]) = -\log(4.0 \times 10^{-13}) = 12.40$$

Finding the pH of a Strong Acid

- there are two sources of H_3O^+ in an aqueous solution of a strong acid – the acid and the water
- for the strong acid, the contribution of the water to the total $[H_3O^+]$ is negligible
  - ✓ shifts the K_w equilibrium to the left so far that $[H_3O^+]_{water}$ is too small to be significant
    - ➢ except in very dilute solutions, generally < 1×10^{-4} M
- for a strong monoprotic acid $[H_3O^+] = [HAcid]$
  - ✓ for polyprotic acids, the other ionizations can *generally* be ignored since they are so much weaker in acid strength

Finding the pH of a Weak Acid

- there are also two sources of H_3O^+ in an aqueous solution of a weak acid
  - the acid and the water
- however, finding the $[H_3O^+]$ is complicated by the fact that the weak acid only undergoes partial ionization
- calculating the $[H_3O^+]$ requires solving an equilibrium problem for the reaction that defines the acidity of the acid

$HAcid + H_2O \Leftrightarrow Acid^- + H_3O^+$

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[H_3O^+]$ from water is ≈ 0

$$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	≈ 0
change			
equilibrium			

o products initially, $Q_c = 0$, and the reaction is proceeding f

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

represent the change in the concentrations in terms of x
sum the columns to find the equilibrium concentrations in terms of x
substitute into the equilibrium constant expression

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	0
change	$-x$	$+x$	$+x$
equilibrium	$0.200 - x$	x	x

$$K_a = \frac{[NO_2][H_3O^+]}{[HNO_2]} = \frac{(x)(x)}{(2.00\times10^{-1} - x)}$$

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

K_a for $HNO_2 = 4.6 \times 10^{-4}$

get the value of K_a from K_a Tables

since K_a is very small, approximate the $[HNO_2]_{eq} = [HNO_2]_{init}$ and solve for x

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	≈ 0
change	0.200 -x	+x	+x
equilibrium	0.200	(x)	(x)

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(x)(x)}{(2.00\times10^{-1} - x)}$$

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(x)(x)}{(2.00\times10^{-1})}$$

$$4.6\times10^{-4} = \frac{x^2}{2.00\times10^{-1}}$$

$$x = \sqrt{(4.6\times10^{-4})(2.00\times10^{-1})}$$

$$x = 9.6\times10^{-3}$$

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

K_a for $HNO_2 = 4.6 \times 10^{-4}$

check if the approximation is valid by seeing if $x < 5\%$ of $[HNO_2]_{init}$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.200	x	x

$x = 9.6 \times 10^{-3}$

$$\frac{9.6\times10^{-3}}{2.00\times10^{-1}}\times100\% = 4.8\% < 5\%$$

the approximation is valid

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

K_a for $HNO_2 = 4.6 \times 10^{-4}$

substitute x into the equilibrium concentration definitions and solve

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.200 - x$	x	x
	0.190	0.009	0.009

$x = 9.6 \times 10^{-3}$

$$[HNO_2] = 0.200 - x = 0.200 - (9.6 \times 10^{-3}) = 0.190\ M$$

$$[NO_2^-] = [H_3O^+] = x = 9.6 \times 10^{-3}\ M$$

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

K_a for $HNO_2 = 4.6 \times 10^{-4}$

substitute $[H_3O^+]$ into the formula for pH and solve

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	≈ 0
change	$-x$	$+x$	$+x$
equilibri	0.190	0.0096	0.0096

$$pH = -\log\left(H_3O^+\right)$$

$$= -\log\left(9.6\times10^{-3}\right) = 2.02$$

Find the pH of 0.200 M $HNO_2(aq)$ solution @ 25°C (weak acid)

K_a for $HNO_2 = 4.6 \times 10^{-4}$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	0.200	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.190	0.0096	0.0096

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} =$$

$$= \frac{(9.6\times10^{-3})^2}{(0.190)} = 4.9\times10^{-4}$$

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a

- although not exact, the answer is reasonably close

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? (K_a = 1.4 x 10^{-5} @ 25°C)

Write the reaction for the acid with water

$HC_6H_4NO_2 + H_2O \Leftrightarrow C_6H_4NO_2^- + H_3O^+$

Construct an ICE table for the reaction

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.012	0	≈ 0
change			
equilibrium			

Enter the initial concentrations – assuming the $[H_3O^+]$ from water is ≈ 0

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? (K_a = 1.4 x 10^{-5} @ 25°C)

represent the change in the concentrations in terms of *x*

sum the columns to find the equilibrium concentrations in terms of *x*

substitute into the equilibrium constant expression

$$HC_6H_4NO_2 + H_2O \Leftrightarrow C_6H_4NO_2^- + H_3O^+$$

	[HA]	[A^-]	[H_3O^+]
initial	0.012	0	0
change	$-x$	$+x$	$+x$
equilibrium	$0.012 - x$	x	x

$$K_a = \frac{[C_6H_4NO_2][H_3O^+]}{[HC_6H_4NO_2]} = \frac{(x)(x)}{(1.2\times10^{-2} - x)}$$

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? $K_a = 1.4 \times 10^{-5}$ @ 25°C

$$HC_6H_4NO_2 + H_2O \Leftrightarrow C_6H_4NO_2^- + H_3O^+$$

determine the value of K_a
since K_a is very small, approximate the $[HA]_{eq} = [HA]_{init}$ and solve for x

	[HA]	$[A_2^-]$	$[H_3O^+]$
initial	0.012	0	≈ 0
change	0.012 -x	$+x$	$+x$
equilibrium	0.012	x	x

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(x)(x)}{(1.2\times10^{-2} - x)} \qquad K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(x)(x)}{(1.2\times10^{-2})}$$

$$1.4\times10^{-5} = \frac{x^2}{1.2\times10^{-2}}$$

$$x = \sqrt{(1.4\times10^{-5})(1.2\times10^{-2})}$$

$$x = 4.1\times10^{-4}$$

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? $K_a = 1.4 \times 10^{-5}$ @ 25°C

K_a for $HC_6H_4NO_2 = 1.4 \times 10^{-5}$

check if the approximation is valid by seeing if $x <$ 5% of $[HC_6H_4NO_2]_{init}$

	[HA]	$[A_2^-]$	$[H_3O^+]$
initial	0.012	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.012	x	x

$x = 4.1 \times 10^{-4}$

$$\frac{4.1\times10^{-4}}{1.2\times10^{-2}} \times 100\% = 3.4\% < 5\%$$

the approximation is valid

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? $K_a = 1.4 \times 10^{-5}$ @ 25°C

$$HC_6H_4NO_2 + H_2O \Leftrightarrow C_6H_4NO_2^- + H_3O$$

substitute x into the equilibrium concentration definitions and solve

	[HA]	$[A_2^-]$	$[H_3O^+]$
initial	0.012	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.012-x$	x	x

$x = 4.1 \times 10^{-4}$

$$\left[HC_6H_4NO_2\right] = 0.012 - x = 0.012 - \left(4.1\times10^{-4}\right) = 0.012\,M$$

$$\left[C_6H_4NO_2^-\right] = \left[H_3O^+\right] = x = 4.1\times10^{-4}\,M$$

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? K_a = 1.4 x 10^{-5} @ 25°C

substitute $[H_3O^+]$ into the formula for pH and solve

	[HA]	$[A_2^-]$	$[H_3O^+]$
initial	0.012	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.012	0.00041	0.00041

$$pH = -\log(H_3O^+)$$

$$= -\log(4.1\times10^{-4}) = 3.39$$

Practice - What is the pH of a 0.012 M solution of nicotinic acid, $HC_6H_4NO_2$? $K_a = 1.4 \times 10^{-5}$ @ 25°C

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a values

- to see if they match

	[HA]	$[A_2^-]$	$[H_3O^+]$
initial	0.012	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.012	0.00041	0.00041

$$K_a = \frac{[C_6H_4NO_2^-][H_3O^+]}{[HC_6H_4NO_2]}$$

$$= \frac{(4.1\times10^{-4})^2}{(1.2\times10^{-2})} = 1.4\times10^{-5}$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[H_3O^+]$ from water is ≈ 0

$$HClO_2 + H_2O \Leftrightarrow ClO_2^- + H_3O^+$$

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change			
equilibrium			

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

represent the change in the concentrations in terms of x
sum the columns to find the equilibrium concentrations in terms of x
substitute into the equilibrium constant expression

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100-x$	x	x

$$K_a = \frac{[ClO_2][H_3O^+]}{[HClO_2]} = \frac{(x)(x)}{(1.00\times10^{-1} - x)}$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for $HClO_2 = 1.1 \times 10^{-2}$

determine the value of K_a from Table 15.5

since K_a is very small, approximate the $[HClO_2]_{eq} = [HClO_2]_{init}$ and solve for x

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100-x$	x	x

$$K_a = \frac{[ClO_2^-][H_3O^+]}{[HClO_2]} = \frac{(x)(x)}{(1.00\times10^{-1})}$$

$$1.1\times10^{-2} = \frac{x^2}{1.00\times10^{-1}}$$

$$x = \sqrt{(1.1\times10^{-2})(1.00\times10^{-1})}$$

$$x = 3.3\times10^{-2}$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for $HClO_2 = 1.1 \times 10^{-2}$

check if the approximation is valid by seeing if $x < 5\%$ of $[HNO_2]_{init}$

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100-x$	x	x

$x = 3.3 \times 10^{-2}$

$$\frac{3.3\times10^{-2}}{1.00\times10^{-1}}\times100\% = 33\% > 5\%$$

the approximation is NOT valid

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for $HClO_2 = 1.1 \times 10^{-2}$

if the approximation is invalid, solve for x using the quadratic formula

$$K_a = \frac{[ClO_2^-][H_3O^+]}{[HClO_2]} = \frac{(x)(x)}{(1.00\times10^{-1} - x)}$$

$$1.1\times10^{-2} = \frac{x^2}{(1.00\times10^{-1} - x)}$$

$$0 = x^2 + 0.011x - 0.0011$$

$$x = \frac{-0.011 \pm \sqrt{(0.011)^2 - 4(1)(-0.0011)}}{2(1)}$$

$$x = 0.028 \text{ or } -0.039$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for $HClO_2$ = 1.1 x 10^{-2}

substitute x into the equilibrium concentration definitions and solve

$x = 0.028$

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100 - x$	x	x

$$[HClO_2] = 0.100 - x = 0.100 - (0.028) = 0.072\ M$$

$$[ClO_2^-] = [H_3O^+] = x = 0.028\ M$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for $HClO_2 = 1.1 \times 10^{-2}$

substitute $[H_3O^+]$ into the formula for pH and solve

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.072	0.028	0.028

$$pH = -\log(H_3O^+)$$

$$= -\log(0.028) = 1.55$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for $HClO_2 = 1.1 \times 10^{-2}$

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a

the answer matches

	$[HClO_2]$	$[ClO_2^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.072	0.028	0.028

$$K_a = \frac{[ClO_2][H_3O^+]}{[HClO_2]} =$$

$$= \frac{(0.028)^2}{(0.072)} = 1.1 \times 10^{-2}$$

What is the K_a of a weak acid if a 0.100 M solution has a pH of 4.25?

Use the pH to find the equilibrium $[H_3O^+]$
Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations and $[H_3O^+]_{equil}$

$$[H_3O^+] = 10^{-pH} = 10^{-4.25} = 5.6 \times 10^{-5}\ M$$

$$HA + H_2O \Leftrightarrow A^- + H_3O^+$$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0	≈ 0
change			
equilibrium			5.6E-05

What is the K_a of a weak acid if a 0.100 M solution has a pH of 4.25?

fill in the rest of the table using the $[H_3O^+]$ as a guide
if the difference is insignificant, i.e. $[HA]_{equil} = [HA]_{initial}$
substitute into the K_a expression and compute K_a

$$HA + H_2O \Leftrightarrow A^- + H_3O^+$$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0	0
change	0.100 − 5.6E-05	+5.6E-05	+5.6E-05
equilibrium	5.6E-05	5.6E-05	5.6E-05

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(5.6\times10^{-5})(5.6\times10^{-5})}{(0.100)}$$

$$K_a = 3.1\times10^{-8}$$

Percent Ionization

- another way to measure the strength of an acid is to determine the percentage of acid molecules that ionize when dissolved in water – this is called the **percent ionization**
  - ✓ the higher the percent ionization, the stronger the acid

$$\text{Percent Ionization} = \frac{\text{concentration of ionized acid at equilibrium}}{\text{initial molarity of acid}} \times 100\%$$

since $[\text{ionized acid}]_{equil} = [H_3O^+]_{equil}$

$$\text{Percent Ionization} = \frac{[H_3O^+]_{equil}}{[HA]_{init}} \times 100\%$$

What is the percent ionization of a 2.5 M HNO_2 solution?

Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the Initial Concentrations
Define the Change in Concentration in terms of *x*
Sum the columns to define the

$$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	2.5	0	≈ 0
change	$2.5 - x$	$+x$	$+x$
equilibrium			

What is the percent ionization of a 2.5 M HNO_2 solution?

determine the value of K_a from Table 15.5

since K_a is very small, approximate the $[HNO_2]_{eq} = [HNO_2]_{init}$ and solve for x

K_a for $HNO_2 = 4.6 \times 10^{-4}$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	2.5	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$2.5-x \approx 2.5$	x	x

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(x)(x)}{(2.5)}$$

$$4.6\times10^{-4} = \frac{x^2}{2.5}$$

$$x = \sqrt{(4.6\times10^{-4})(2.5)}$$

$$x = 3.4\times10^{-2}$$

What is the percent ionization of a 2.5 M HNO_2 solution?

$$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	2.5	0	≈ 0
change	2.5 - x	x	x
equilibri	2.5	0.034	0.034

substitute x into the Equilibrium Concentration definitions and solve

$x = 3.4 \times 10^{-2}$

$[HNO_2] = 2.5 - x = 2.5 - (0.034) = 2.5\,M$

$[NO_2^-] = [H_3O^+] = x = 0.034\,M$

What is the percent ionization of a 2.5 M HNO_2 solution?

Apply the Definition and Compute the Percent Ionization

$$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$$

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
initial	2.5	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	2.5	0.034	0.034

$$\text{Percent Ionization} = \frac{[H_3O^+]_{equil}}{[HNO_2]_{init}} \times 100\%$$

since the percent ionization is < 5%, the "x is small" approximation is valid

$$= \frac{3.4 \times 10^{-2}}{2.5} \times 100\% = 1.4\%$$

Why doesn't the increase in H_3O^+ keep up with the increase in HA?

- the reaction for ionization of a weak acid is:

$$HA_{(aq)} + H_2O_{(l)} \Leftrightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

- according to Le Châtelier's Principle, if we reduce the concentrations of all the (*aq*) components, the equilibrium should shift to the right to increase the total number of dissolved particles
  - ✓ we can reduce the (*aq*) concentrations by using a more dilute initial acid concentration
- the result will be a larger $[H_3O^+]$ in the dilute solution compared to the initial acid concentration
- this will result in a larger percent ionization

Finding the pH of Mixtures of Acids

- generally, you can ignore the contribution of the weaker acid to the $[H_3O^+]_{equil}$
- for a mixture of a strong acid with a weak acid, the complete ionization of the strong acid provides more than enough $[H_3O^+]$ to shift the weak acid equilibrium to the left so far that the weak acid's added $[H_3O^+]$ is negligible
- for mixtures of weak acids, generally only need to consider the stronger for the same reasons
  - ✓ as long as one is significantly stronger than the other, and their concentrations are similar

Find the pH of a mixture of 0.150 M HF(aq) solution and 0.100 M $HClO_2$(aq)

Write the reactions for the acids with water and determine their K_as
If the K_as are sufficiently different, use the strongest acid to construct an ICE table for the reaction
Enter the initial concentrations –

$HF + H_2O \Leftrightarrow F^- + H_3O^+ \quad K_a = 3.5 \times 10^{-4}$

$HClO_2 + H_2O \Leftrightarrow ClO_2^- + H_3O^+ \quad K_a = 2.9 \times 1$

$H_2O + H_2O \Leftrightarrow OH^- + H_3O^+ \quad K_w = 1.0 \times 1$

	[HF]	[F^-]	[H_3O^+]
initial	0.150	0	≈ 0
change			
equilibrium			

Find the pH of a mixture of 0.150 M HF(aq) solution and 0.100 M $HClO_2$(aq)

represent the change in the concentrations in terms of x
sum the columns to find the equilibrium concentrations in terms of x
substitute into the equilibrium constant expression

	[HF]	[F^-]	[H_3O^+]
initial	0.150	0	0
change	$-x$	$+x$	$+x$
equilibrium	$0.150 - x$	x	x

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(x)(x)}{(1.50\times10^{-1} - x)}$$

Find the pH of a mixture of 0.150 M HF(aq) solution and 0.100 M $HClO_2$(aq)

K_a for HF = 3.5 x 10^{-4}

determine the value of K_a for HF
since K_a is very small, approximate the $[HF]_{eq} = [HF]_{init}$ and solve for x

	[HF]	[F^-]	[H_3O^+]
initial	0.150	0	≈ 0
change	0.150 -x	+x	+x
equilibrium	0.150	x	x

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(x)(x)}{(0.150 - x)} \qquad K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(x)(x)}{(0.150)}$$

$$3.5\times10^{-4} = \frac{x^2}{1.50\times10^{-1}}$$

$$x = \sqrt{(3.5\times10^{-4})(1.50\times10^{-1})}$$

$$x = 7.2\times10^{-3}$$

Find the pH of a mixture of 0.150 M HF(aq) solution and 0.100 M $HClO_2$(aq)

K_a for HF = 3.5 x 10^{-4}

check if the approximation is valid by seeing if x < 5% of $[HF]_{init}$

	[HF]	$[F^-]$	$[H_3O^+]$
initial	0.150	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.150	x	x

$x = 7.2 \times 10^{-3}$

$$\frac{7.2\times10^{-3}}{1.50\times10^{-1}}\times100\% = 4.8\% < 5\%$$

the approximation is valid

Find the pH of a mixture of 0.150 M HF(aq) solution and 0.100 M $HClO_2$(aq)

K_a for HF = 3.5 x 10^{-4}

substitute x into the equilibrium concentration definitions and solve

	[HF]	[F^-]	[H_3O^+]
initial	0.150	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.150-x$	x	x
	$0.150-7.2\times10^{-3}$	0.007	0.007
	0.143	$\approx x$	$\approx x$

$x = 7.2 \times 10^{-3}$

$$\left[HF\right] = 0.150 - x = 0.150 - \left(7.2\times10^{-3}\right) = 0.143\ M$$

$$\left[F^-\right] = \left[H_3O^+\right] = x = 7.2\times10^{-3}\ M$$

Find the pH of a mixture of 0.150 M HF(*aq*) solution and 0.100 M $HClO_2$(*aq*)

K_a for HF = 3.5 x 10^{-4}

substitute $[H_3O^+]$ into the formula for pH and solve

	[HF]	$[F^-]$	$[H_3O^+]$
initial	0.150	0	≈ 0
change	-*x*	+*x*	+*x*
equilibri	0.143	0.007 2	0.007 2

$$pH = -\log\left(H_3O^+\right)$$

$$= -\log\left(7.2\times10^{-3}\right) = 2.14$$

Find the pH of a mixture of 0.150 M HF(aq) solution and 0.100 M $HClO_2$(aq)

K_a for HF = 3.5 x 10^{-4}

	[HF]	[F^-]	[H_3O^+]
initial	0.150	0	≈ 0
change	-x	+x	+x
equilibrium	0.143	0.0072	0.0072

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(7.2\times10^{-3})^2}{(0.143)} = 3.6\times10^{-4}$$

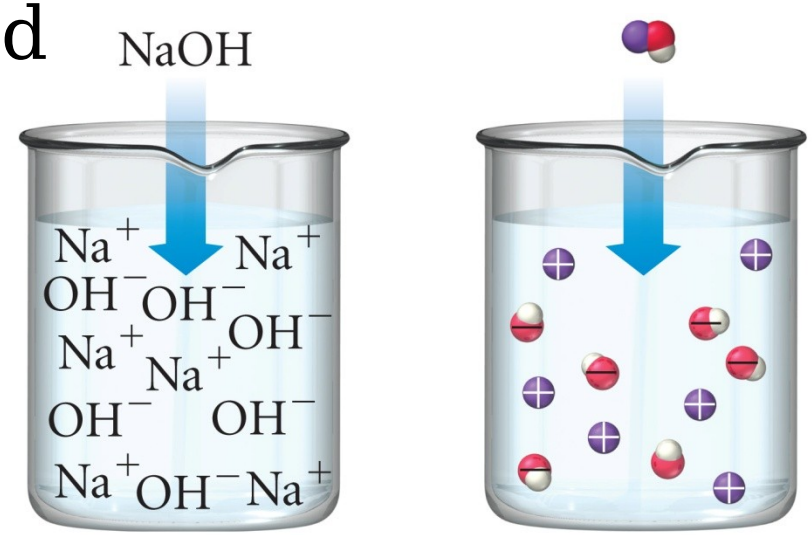
check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a

- although not exact, the answer is reasonably close

Strong Bases

- the stronger the base, the more willing it is to accept H
  - ✓use water as the standard acid
- for strong bases, practically all molecules are dissociated into OH- or accept H's
  - ✓strong electrolyte
  - ✓multi-OH strong bases completely dissociated
- [HO-] = [strong base] x (# OH)

$NaOH \rightarrow Na^+ + OH^-$



Calculate the pH at 25°C of a 0.0015 M $Sr(OH)_2$ solution and determine if the solution is acidic, basic, or neutral

Given: $[Sr(OH)_2] = 1.5 \times 10^{-3}$ M

Find: pH

Concept Plan: $[Sr(OH)_2] \rightarrow [OH^-] \rightarrow [H_3O^+] \rightarrow pH$

$[OH^-] = 2[Sr(OH)_2]$ $K_w = [H_3O^+][OH^-]$ $pH = -\log[H_3O^+]$

Relationships:

Solution:

$[OH^-] = 2(0.0015) = 0.0030$ M

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-3}}$$

$$[H_3O^+] = 3.3 \times 10^{-12} \text{ M}$$

$$pH = -\log(3.3 \times 10^{-12})$$

$$pH = 11.48$$

Check: pH is unitless. The fact that the pH > 7 means the solution is basic

Calculate the pH of a 0.0010 M $Ba(OH)_2$ solution and determine if it is acidic, basic, or neutral

$Ba(OH)_2 = Ba^{2+} + 2\ OH^-$ therefore

$[OH^-] = 2 \times 0.0010 = 0.0020 = 2.0 \times 10^{-3}\ M$

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} M$$

$$pH = -\log [H_3O^+] = -\log (5.0 \times 10^{-12})$$

$$pH = 11.30$$

$pH > 7$ therefore **basic**

Weak Bases

- in weak bases, only a small fraction of molecules accept H's
  - ✓weak electrolyte
  - ✓most of the weak base molecules do not take H from water
  - ✓much less than 1% ionization in water
- [HO-] << [weak base]
- finding the pH of a weak base solution is similar to finding th pH of a weak acid

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + O$$

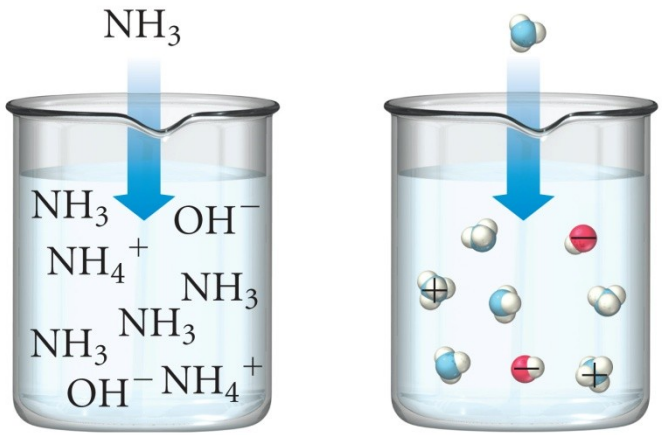


TABLE 15.8 Some Common Weak Bases

Weak Base	Ionization Reaction	K_b
Carbonate ion (CO_3^{2-})*	$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$	1.8×10^{-4}
Methylamine (CH_3NH_2)	$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$	4.4×10^{-4}
Ethylamine ($C_2H_5NH_2$)	$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$	5.6×10^{-4}
Ammonia (NH_3)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	1.76×10^{-5}
Pyridine (C_5H_5N)	$C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$	1.7×10^{-9}
Bicarbonate ion (HCO_3^-)* (or hydrogen carbonate)	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	1.7×10^{-9}
Aniline ($C_6H_5NH_2$)	$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$	3.9×10^{-10}

*The carbonate and bicarbonate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate ($NaHCO_3$) basic. We look more closely at ionic bases in Section 15.8.

Find the pH of 0.100 M $NH_3(aq)$ solution

Write the reaction for the base with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[OH^-]$ from water is ≈ 0

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	≈ 0
change			
equilibrium			

o products initially, $Q_c = 0$, and the reaction is proceeding f

Find the pH of 0.100 M $NH_3(aq)$ solution

represent the change in the concentrations in terms of x
sum the columns to find the equilibrium concentrations in terms of x
substitute into the equilibrium constant expression

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	0
change	$-x$	$+x$	$+x$
equilibrium	$0.100 - x$	x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{(1.00\times10^{-1} - x)}$$

Find the pH of 0.100 M $NH_3(aq)$ solution

K_b for NH_3 = 1.76 x 10^{-5}

determine the value of K_b from Table 15.8

since K_b is very small, approximate the $[NH_3]_{eq} = [NH_3]_{init}$ and solve for x

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	≈ 0
change	0.100 -x	$+x$	$+x$
equilibrium	0.100	x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{(1.00\times10^{-1} - x)} \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{(1.00\times10^{-1})}$$

$$1.76\times10^{-5} = \frac{x^2}{1.00\times10^{-1}}$$

$$x = \sqrt{(1.76\times10^{-5})(1.00\times10^{-1})}$$

$$x = 1.33\times10^{-3}$$

Find the pH of 0.100 M $NH_3(aq)$ solution

K_b for NH_3 = 1.76 x 10^{-5}

check if the approximation is valid by seeing if x < 5% of $[NH_3]_{init}$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibri um	0.100	x	x

$x = 1.33 \times 10^{-3}$

$$\frac{1.33\times10^{-3}}{1.00\times10^{-1}}\times100\% = 1.33\% < 5\%$$

the approximation is valid

Find the pH of 0.100 M $NH_3(aq)$ solution

K_b for NH_3 = 1.76 x 10^{-5}

substitute x into the equilibrium concentration definitions and solve

$x = 1.33 \times 10^{-3}$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100 $-x$	1.33E-3 x	1.33E-3 x

$$[NH_3] = 0.100 - x = 0.100 - (1.33 \times 10^{-3}) = 0.099\ M$$

$$[NH_4^+] = [OH^-] = x = 1.33 \times 10^{-3}\ M$$

Find the pH of 0.100 M $NH_3(aq)$ solution

K_b for NH_3 = 1.76 x 10^{-5}

use the $[OH^-]$ to find the $[H_3O^+]$ using K_w
substitute $[H_3O^+]$ into the formula for pH and solve

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.099	1.33E-3	1.33E-3

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{1.33 \times 10^{-3}}$$

$$[H_3O^+] = 7.52 \times 10^{-12}$$

$$pH = -\log(H_3O^+)$$

$$= -\log(7.52 \times 10^{-12}) = 11.124$$

Find the pH of 0.100 M $NH_3(aq)$ solution

K_b for NH_3 = 1.76 x 10^{-5}

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.099	1.33E-3	1.33E-3

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{(1.33\times10^{-3})^2}{(0.099)} = 1.8\times10^{-5}$$

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_b to the given K_b

though not exact, the answer is reasonably close

Practice – Find the pH of a 0.0015 M morphine solution, $K_b = 1.6 \times 10^{-6}$

Write the reaction for the base with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[OH^-]$ from water is ≈ 0

$$B + H_2O \Leftrightarrow BH^+ + OH^-$$

	[B]	$[BH^+]$	$[OH^-]$
initial	0.0015	0	≈ 0
change			
equilibrium			

o products initially, $Q_c = 0$, and the reaction is proceeding f

Practice – Find the pH of a 0.0015 M morphine solution

represent the change in the concentrations in terms of *x*
sum the columns to find the equilibrium concentrations in terms of *x*
substitute into the equilibrium constant expression

	[B]	[BH^+]	[OH^-]
initial	0.0015	0	0
change	$-x$	$+x$	$+x$
equilibrium	$0.0015 - x$	x	x

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(x)(x)}{(1.5\times10^{-3} - x)}$$

Practice – Find the pH of a 0.0015 M morphine solution

determine the value of K_b
since K_b is very small, approximate the $[B]_{eq} = [B]_{init}$ and solve for x

K_b for Morphine = 1.6×10^{-6}

	[B]	$[BH^+]$	$[OH^-]$
initial	0.0015	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.0015 - x$	x	x

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(x)(x)}{(1.5\times10^{-3} - x)}$$

5

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(x)(x)}{(1.5\times10^{-3})}$$

$$1.6\times10^{-6} = \frac{x^2}{1.5\times10^{-1}}$$

$$x = \sqrt{(1.6\times10^{-6})(1.5\times10^{-3})}$$

$$x = 4.9\times10^{-5}$$

Practice – Find the pH of a 0.0015 M morphine solution

K_b for Morphine = 1.6×10^{-6}

check if the approximation is valid by seeing if $x < 5\%$ of $[B]_{init}$

	[B]	$[BH^+]$	$[OH^-]$
initial	0.0015	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.0015	x	x

$x = 4.9 \times 10^{-5}$

$$\frac{4.9\times10^{-5}}{1.5\times10^{-3}}\times100\% = 3.3\% < 5\%$$

the approximation is valid

Practice – Find the pH of a 0.0015 M morphine solution

K_b for Morphine = 1.6 x 10^{-6}

substitute x into the equilibrium concentration definitions and solve

$x = 4.9 \times 10^{-5}$

	[B]	[BH^+]	[OH^-]
initial	**0.0015**	**0**	**≈ 0**
change	**-*x***	**+*x***	**+*x***
equilibrium	0.0015 -*x*	4.9E-5 *x*	4.9E-5 *x*

$$[\text{Morphine}] = 0.0015 - x = 0.0015 - (4.9\times10^{-5}) = 0.0015\ \text{M}$$

$$[BH^+] = [OH^-] = x = 4.9\times10^{-5}\ \text{M}$$

Practice – Find the pH of a 0.0015 M morphine solution

K_b for Morphine = 1.6 x 10^{-6}

use the $[OH^-]$ to find the $[H_3O^+]$ using K_w
substitute $[H_3O^+]$ into the formula for pH and solve

	[B]	$[BH^+]$	$[OH^-]$
initial	0.0015	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.0015	4.9E-5	4.9E-5

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{1.00\times10^{-14}}{4.9\times10^{-5}}$$

$$[H_3O^+] = 2.0\times10^{-10}$$

$$pH = -\log(H_3O^+)$$

$$= -\log(2.0\times10^{-10}) = 9.69$$

Practice – Find the pH of a 0.0015 M morphine solution

K_b for Morphine = 1.6 x 10^{-6}

	[B]	[BH^+]	[OH^-]
initial	0.0015	0	≈ 0
change	-x	+x	+x
equilibrium	0.0015	4.9E-5	4.9E-5

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_b to the given K_b

the answer matches the given K_b

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$= \frac{(4.9\times10^{-5})^2}{(0.0015)} = 1.6\times10^{-6}$$

Acid-Base Properties of Salts

salts are water soluble ionic compounds

Salts that do not react appreciably with water to produce either H_3O^{1+} or OH^{1-} ions, yield neutral solutions, e.g.

- **Cations from strong bases**:
  - ✓ Alkali metal cations of group 1a (Li^{1+}, Na^{1+}, K^{1+})
  - ✓ Alkaline earth metal cations of group 2a (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), except for Be^{2+}

- **Anions from strong monoprotic acids**:
  - ✓ Cl^{1-}, Br^{1-}, I^{1-}, NO_3^{1-}, and ClO_4^{1-}

Acid-Base Properties of Salts

Salts That Yield Acidic Solutions

- Salts such as NH_4Cl, the conjugate acid derived from a weak base (NH_3) and a strong acid (HCl) yield acidic solutions. Chloride ion (Cl^{1-}) is neither acidic nor basic.

$$NH_4^{1+}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + NH_3(aq)$$

- Hydrated cations of small, highly charged metal ions, such as Al^{3+}.
  - ✓ The acidity of hydrated main-group cations INCREASES from left to right in the periodic table as the metal ion charge increases and the metal ion size decreases:

    $Li^{1+} < Be^{2+}$

    $Na^{1+} < Mg^{2+} < Al^{3+}$

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \Leftrightarrow Al(H_2O)_5(OH)^{2+}(aq) + H_3O^{+}(aq)$$

Acid-Base Properties of Salts

Salts That Yield Basic Solutions

Salts such as NaCN that are derived from a strong base (NaOH) and a weak acid (HCN) yield basic solutions. Sodium ion (Na^{1+}) is neither acidic nor basic.

$$NaCN(aq) + H_2O(l) \rightleftharpoons HCN(aq) + NaOH(aq)$$

Removing the spectator ions gives:

$$CN^{1-}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{1-}(aq)$$

Other examples: NaF $Ca(C_2H_3O_2)_2$ KNO_2

Anions as Weak Bases

- every anion can be thought of as the conjugate base of an acid
- therefore, every anion can potentially be a base
  - ✓ $A^-(aq) + H_2O(l) \Leftrightarrow HA(aq) + OH^-(aq)$
- **the stronger the acid is, the weaker the conjugate base is**
  - ✓ an anion that is the conjugate base of a strong acid is pH neutral

$$Cl^-(aq) + H_2O(l) \leftarrow HCl(aq) + OH^-(aq)$$

    - ➢ since HCl is a strong acid, this equilibrium lies practically completely to the left
  - ✓ an anion that is the conjugate base of a weak acid is basic

$$F^-(aq) + H_2O(l) \Leftrightarrow HF(aq) + OH^-(aq)$$

    - ➢ since HF is a weak acid, the position of this equilibrium favors the right

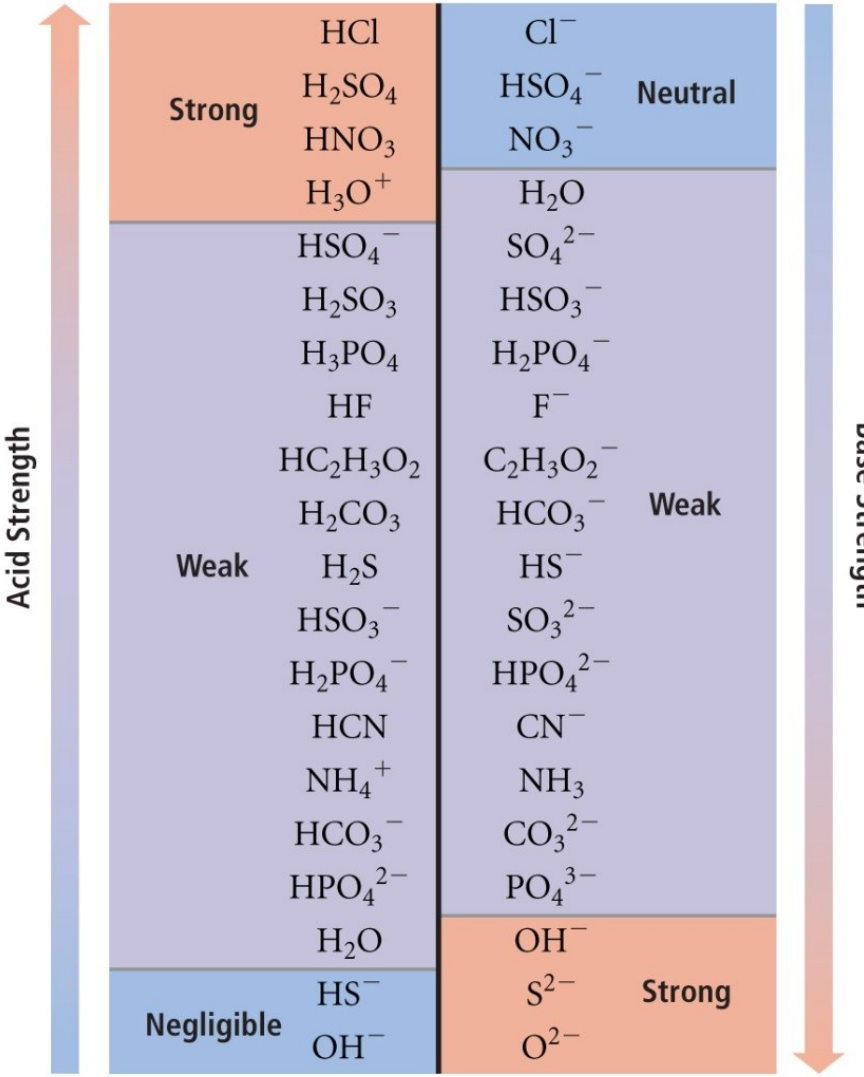
Use the Table to Determine if the Given Anion Is Basic or Neutral

a) NO_3^-

the conjugate base of a strong acid, therefore neutral

b) NO_2^-

the conjugate base of a weak acid, therefore basic



Relationship between K_a of an Acid and K_b of Its Conjugate Base

- many reference books only give tables of K_a values because K_b values can be found from them

when you add equations, you multiply the K's

$$\cancel{HA(aq)} + H_2O(l) \Leftrightarrow \cancel{A^-(aq)} + H_3O^+(aq) \qquad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$\cancel{A^-(aq)} + H_2O(l) \Leftrightarrow \cancel{HA(aq)} + OH^-(aq) \qquad K_b = \frac{[HA][H_3O^+]}{[A^-]}$$

$$2H_2O(l) \Leftrightarrow H_3O^+(aq) + OH^-(aq)$$

$$K_a \times K_b = \frac{\cancel{[A^-]}[H_3O^+]}{\cancel{[HA]}} \times \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}$$

$$K_a \times K_b = [H_3O^+][OH^-] = K_w$$

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

Na^+ is the cation of a strong base – pH neutral. The CHO_2^- is the anion of a weak acid – pH basic
Write the reaction for the anion with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[OH^-]$ from water

$$CHO_2^- + H_2O \Leftrightarrow HCHO_2 + OH^-$$

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change			
equilibrium			

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

represent the change in the concentrations in terms of x

sum the columns to find the equilibrium concentrations in terms of x

Calculate the value of K_b from the value of K_a of the weak acid from Table 15.5

substitute into

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100 - x$	x	x

$$K_a \times K_b = K_w$$

$$K_b = \frac{1.0\times10^{-14}}{1.8\times10^{-4}} = 5.6\times10^{-11}$$

$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]} = \frac{(x)(x)}{(1.00\times10^{-1} - x)}$$

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

K_b for CHO_2^- = 5.6 x 10^{-11}

since K_b is very small, approximate the $[CHO_2^-]_{eq} = [CHO_2^-]_{init}$ and solve for x

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100 - x$	x	x

$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]} = \frac{(x)(x)}{(1.00\times10^{-1} - x)} \qquad K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]} = \frac{(x)(x)}{(1.00\times10^{-1})}$$

$$5.6\times10^{-11} = \frac{x^2}{1.00\times10^{-1}}$$

$$x = \sqrt{(5.6\times10^{-11})(1.00\times10^{-1})}$$

$$x = 2.4\times10^{-6}$$

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

K_b for CHO_2^- = 5.6 x 10^{-11}

check if the approximation is valid by seeing if x < 5% of $[CHO_2^-]_{init}$

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100	x	x

$x = 2.4 \times 10^{-6}$

$$\frac{2.4\times10^{-6}}{1.00\times10^{-1}}\times100\% = 0.0024\% < 5\%$$

the approximation is valid

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

K_b for CHO_2^- = 5.6 x 10^{-11}

substitute x into the equilibrium concentration definitions and solve

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100 $-x$	2.4E-6 x	2.4E-6 x

$x = 2.4 \times 10^{-6}$

$$\left[CHO_2^-\right] = 0.100 - x = 0.100 - \left(2.4\times10^{-6}\right) = 0.100\ M$$

$$[HCHO_2] = [OH^-] = x = 2.4\times10^{-6}\ M$$

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

K_b for CHO_2^- = 5.6 x 10^{-11}

use the $[OH^-]$ to find the $[H_3O^+]$ using K_w
substitute $[H_3O^+]$ into the formula for pH and solve

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100	2.4E-6	2.4E-6

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{1.00\times10^{-14}}{2.4\times10^{-6}}$$

$$[H_3O^+] = 4.2\times10^{-9}$$

$$pH = -\log(H_3O^+)$$

$$= -\log(4.2\times10^{-9}) = 8.38$$

Find the pH of 0.100 M $NaCHO_2(aq)$ solution

K_b for CHO_2^- = 5.6 x 10^{-11}

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
initial	0.100	0	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100	2.4E-6	2.4E-6

$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]}$$

$$= \frac{(2.4\times10^{-6})^2}{(0.100)} = 5.8\times10^{-11}$$

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_b to the given K_b, though not exact, the answer is reasonably close

Acid-Base Properties of Salts

Salts That Contain Acidic Cations and Basic Anions

The pH of an ammonium carbonate solution, $(NH_4)_2CO_3$, depends on the relative acid strength of the cation and the relative base strength of the anion.

Is it *acidic* or *basic*?

Acid-Base Properties of Salts

Salts That Contain Acidic Cations and Basic Anions

$(NH_4)_2CO_3$:

$NH_4^{1+}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + NH_3(aq)$ $\quad K_a = ?$

$K_b = 1.8E\text{-}5$

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{1-}(aq) + OH^{1-}(aq)$ $\quad K_b = ?$

$K_a = 5.6E\text{-}11$

Three possibilities:

- $\boldsymbol{K_a > K_b}$: The solution contains excess H_3O^{1+} ions (pH < 7).
- $\boldsymbol{K_a < K_b}$: The solution contains excess OH^{1-} ions (pH > 7).
- $\boldsymbol{K_a \approx K_b}$: The solution contains $[H_3O^{1+}] \approx [OH^{1-}]$ (pH

Acid-Base Properties of Salts

$(NH_4)_2CO_3$

$$NH_4^{1+}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + NH_3(aq) \quad K_a$$

$$K_a \text{ for } NH_4^{1+} = \frac{K_w}{K_b \text{ for } NH_3} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{1-}(aq) + OH^{1-}(aq) \quad K_b$$

$$K_b \text{ for } CO_3^{2-} = \frac{K_w}{K_a \text{ for } HCO_3^{1-}} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = \boxed{1.8 \times 10^{-4}}$$

Since $K_b > K_a$ the solution will be basic

Acid-Base Properties of Salts

TABLE 14.5 Acid–Base Properties of Salts

Type of Salt	Examples	Ions That React with Water	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KNO_3, BaI_2	None	~7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3, $[(CH_3)_3NH]Cl$	Cation	<7
Small, highly charged cation; anion from strong acid	$AlCl_3$, $Cr(NO_3)_3$, $Fe(ClO_4)_3$	Hydrated cation	<7
Cation from strong base; anion from weak acid	NaCN, KF, Na_2CO_3	Anion	>7
Cation from weak base; anion from weak acid	NH_4CN, NH_4F, $(NH_4)_2CO_3$	Cation and anion	<7 if $K_a > K_b$ >7 if $K_a < K_b$ ~7 if $K_a \approx K_b$

Determine if the Given Cation Is Acidic or Neutral

a) $C_5N_5NH_2^+$

the conjugate acid of a weak base, therefore acidic

- Ca^{2+}

the counterion of a strong base, therefore neutral

- Cr^{3+}

a highly charged metal ion, therefore acidic

Determine whether a solution of the following salts is acidic, basic, or neutral (stop)

a) $SrCl_2$

Sr^{2+} is the counterion of a strong base, pH neutral

Cl^- is the conjugate base of a strong acid, pH neutral

solution will be pH neutral

- $AlBr_3$

  Al^{3+} is a small, highly charged metal ion, weak acid

  Br^- is the conjugate base of a strong acid, pH neutral

  solution will be acidic

- $CH_3NH_3NO_3$

  $CH_3NH_3^+$ is the conjugate acid of a weak base, acidic

  NO_3^- is the conjugate base of a strong acid, pH neutral

  solution will be acidic

Determine whether a solution of the following salts is acidic, basic, or neutral

d) $NaCHO_2$

Na^+ is the counterion of a strong base, pH neutral

CHO_2^- is the conjugate base of a weak acid, basic

solution will be basic

- NH_4F

NH_4^+ is the conjugate acid of a weak base, acidic

F^- is the conjugate base of a weak acid, basic

$K_a(NH_4^+) > K_b(F^-)$; solution will be acidic

Find the pH of 0.0100 M $H_2SO_4(aq)$ solution @ 25°C

Write the reactions for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[HSO_4^-]$ and $[H_3O^+]$ is ≈ $[H_2SO_4]$

$$H_2SO_4 + H_2O \Leftrightarrow HSO_4^- + H_3O^+$$

$$HSO_4^- + H_2O \Leftrightarrow SO_4^{2-} + H_3O^+$$

	$[HSO_4^-]$	$[SO_4^{2-}]$	$[H_3O^+]$
initial	0.0100	0	0.0100
change			
equilibrium			

Find the pH of 0.0100 M $H_2SO_4(aq)$ solution @ 25°C

represent the change in the concentrations in terms of x
sum the columns to find the equilibrium concentrations in terms of x
substitute into the equilibrium constant expression

	$[HSO_4^-]$	$[SO_4^{2-}]$	$[H_3O^+]$
initial	0.0100	0	0.0100
change	$-x$	$+x$	$+x$
equilibrium	$0.0100 - x$	x	$0.0100 + x$

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(x)(0.0100 + x)}{(0.0100 - x)}$$

Find the pH of 0.0100 M $H_2SO_4(aq)$ solution @ 25°C

K_a for HSO_4^- = 0.012

expand and solve for x using the quadratic formula

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(x)(0.0100 + x)}{(0.0100 - x)}$$

$$0.012 = \frac{(0.0100 + x)x}{(0.0100 - x)}$$

$$1.2\times10^{-4} - 1.2\times10^{-2}x = 1.00\times10^{-2}x + x^2$$

$$0 = x^2 + 0.022x - 0.00012$$

$$x = \frac{-0.022 \pm \sqrt{(0.022)^2 - 4(1)(-0.00012)}}{2(1)}$$

$$x = -0.027 \text{ or } 0.0045$$

Find the pH of 0.0100 M $H_2SO_4(aq)$ solution @ 25°C

K_a for HSO_4^- = 0.012

substitute x into the equilibrium concentration definitions and solve

	$[HSO_4^-]$	$[SO_4^{2-}]$	$[H_3O^+]$
initial	0.0100	0	0.0100
change	$-x$	$+x$	$+x$
equilibrium	$0.0100 - x$ 0.0055	$0.0045 + x$ 0.0045	$0.0100 + x$ 0.0145

$x = 0.0045$

$$[HSO_4^-] = 0.0100 - x = 0.0100 - (0.0045) = 0.0055\ M$$

$$[H_3O^+] = (0.0100 + x) = 0.0145\ M$$

$$[SO_4^{2-}] = x = 0.0045\ M$$

Find the pH of 0.0100 M $H_2SO_4(aq)$ solution @ 25°C

K_a for HSO_4^- = 0.012

substitute $[H_3O^+]$ into the formula for pH and solve

	$[HSO_4^-]$	$[SO_4^{2-}]$	$[H_3O^+]$
initial	0.0100	0	0.0100
change	$-x$	$+x$	$+x$
equilibrium	0.0055	0.0045	0.0145

$$pH = -\log(H_3O^+)$$

$$= -\log(0.0145) = 1.839$$

Find the pH of 0.100 M $HClO_2(aq)$ solution @ 25°C

K_a for HSO_4^- = 0.012

	$[HSO_4^-]$	$[SO_4^{2-}]$	$[H_3O^+]$
initial	0.0100	0	0.0100
change	$-x$	$+x$	$+x$
equilibrium	0.0055	0.0045	0.0145

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a

the answer matches

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(0.0045)(0.0145)}{(0.0055)} = 1.2\times10^{-2}$$

Lewis Acids and Bases

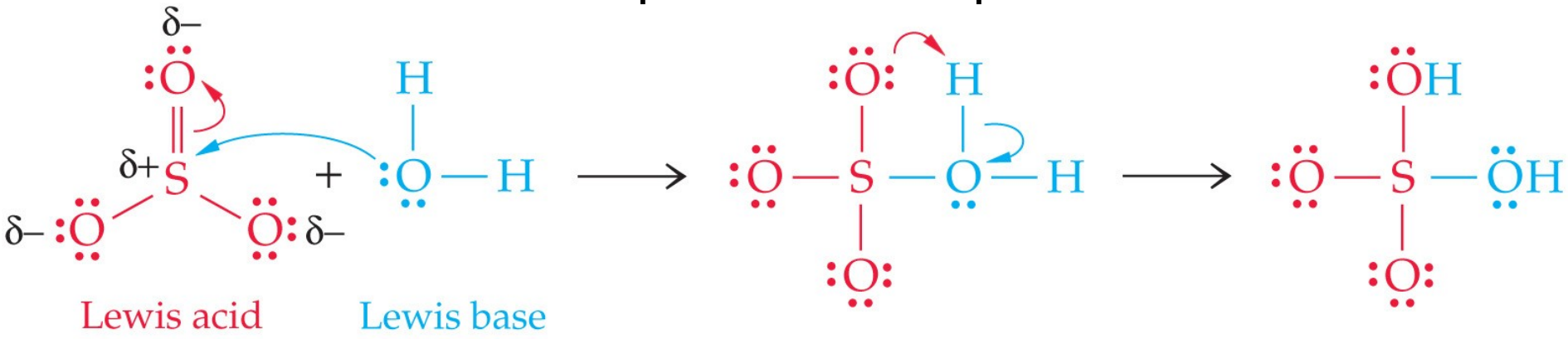
Lewis Acid: An electron-pair acceptor (electrophile).

- electron deficient

Lewis Base: An electron-pair donor (nucleophile).

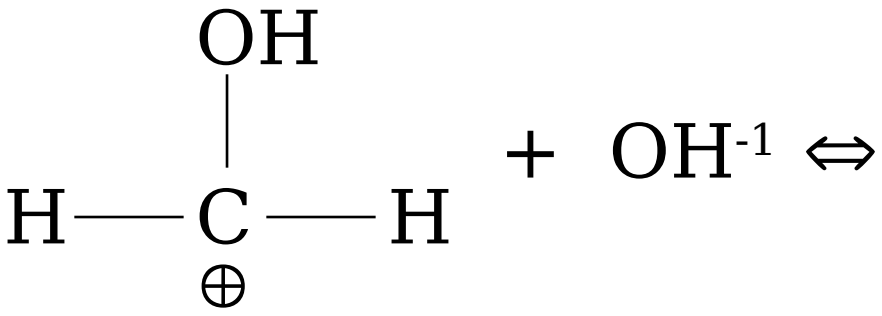
- must have a lone pair of electrons

Nucleophile**:** **+** Electrophile ⇔
Nucleophile**:**Electrophile

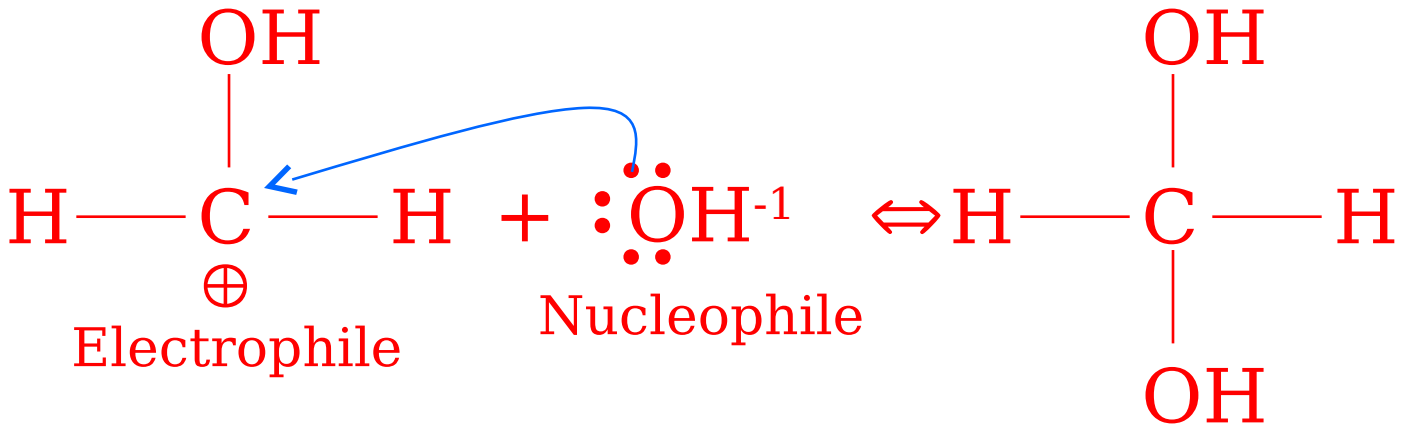


ADDUCT

Complete the Lewis Acid-Base Reaction and Label the Nucleophile & Electrophile



+ OH^{-1} ⇔



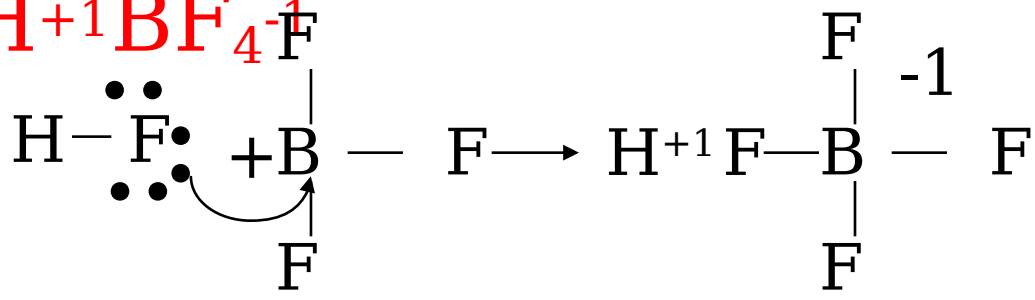
Lewis Acid-Base Reactions Label the Nucleophile and Electrophile

- $BF_3 + HF \Leftrightarrow$
- $CaO + SO_3 \Leftrightarrow$
- $KI + I_2 \Leftrightarrow$

Lewis Acid-Base Reactions Label the Nucleophile and Electrophile

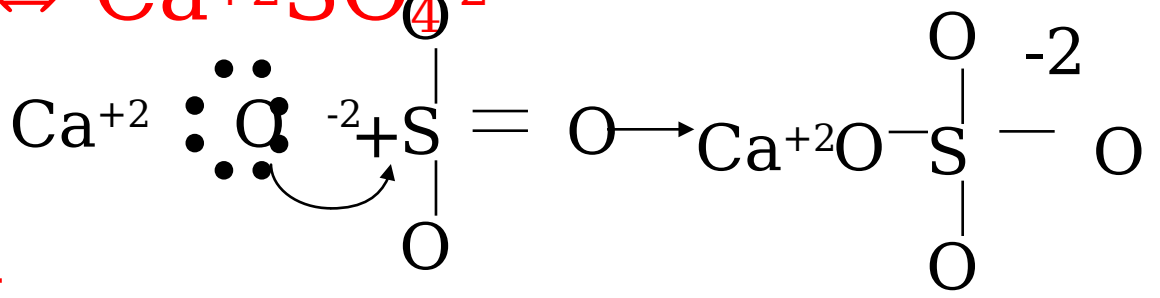
- $BF_3 + HF \Leftrightarrow H^{+1}BF_4^{-1}$

  Elec Nuc



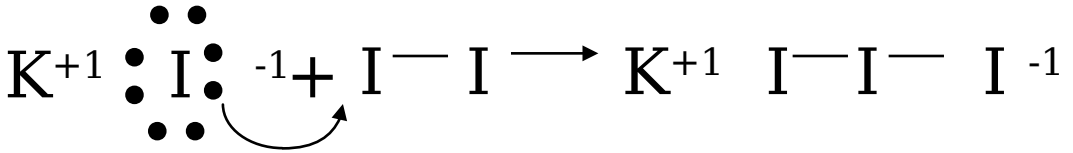
- $CaO + SO_3 \Leftrightarrow Ca^{+2}SO_4^{-2}$

  Nuc Elec



- $KI + I_2 \Leftrightarrow KI_3$

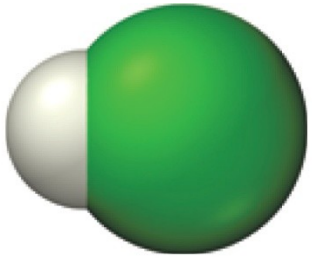
  Nuc Elec



Structures of Acids

- binary acids have acidic hydrogen attached to a nonmetal atom
  - ✓HCl, HF, HBr, HI

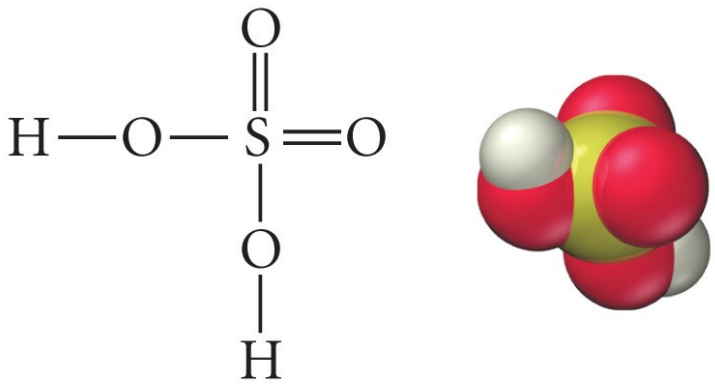
HCl



Hydrochloric acid

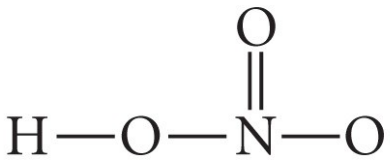
Structure of Acids

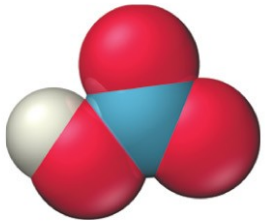
- oxy acids have acidic hydrogen attached to an oxygen atom
  - ✓ H_2SO_4, HNO_3
  - ✓ more oxygen => stronger acid (within a series)



H_2SO_4

Sulfuric Acid



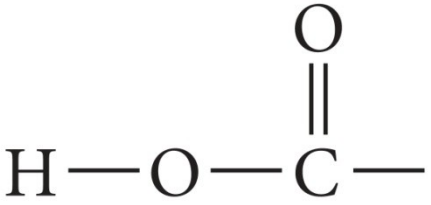


HNO_3

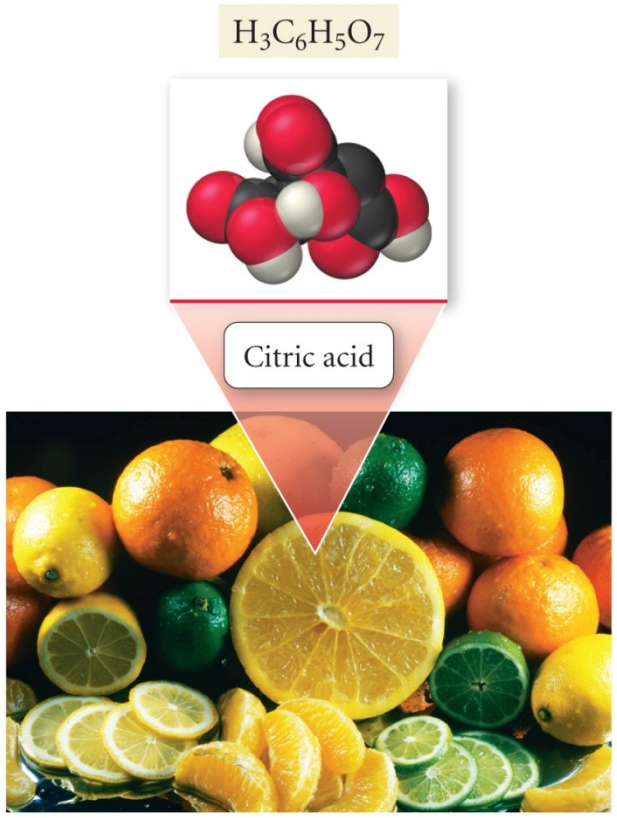
Nitric Acid

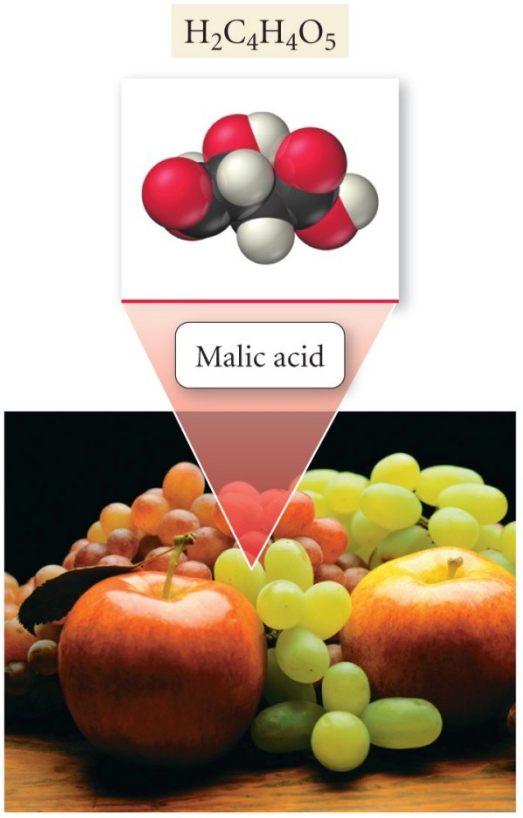
Structure of Acids

- carboxylic acids have COOH group
  - ✓ $HC_2H_3O_2$, $H_3C_6H_5O_7$
- only H attached to oxygen is acidic
- are weak acids



Carboxylic acid group





Common Acids

Chemical Name	Formula	Uses	Strength
Nitric Acid	HNO_3	explosive, fertilizer, dye, glue	Strong
Sulfuric Acid	H_2SO_4	explosive, fertilizer, dye, glue, batteries	Strong
Hydrochloric Acid	HCl	metal cleaning, food prep, ore refining, stomach acid	Strong
Phosphoric Acid	H_3PO_4	fertilizer, plastics & rubber, food preservation	Moderate
Acetic Acid	$HC_2H_3O_2$	plastics & rubber, food preservation, Vinegar	Weak
Hydrofluoric Acid	HF	metal cleaning, glass etching	Weak
Carbonic Acid	H_2CO_3	soda water	Weak
Boric Acid	H_3BO_3	eye wash	Weak

Structure of Bases

- most ionic bases contain OH ions
  - ✓ $NaOH$, $Ca(OH)_2$
- some contain CO_3^{2-} ions
  - ✓ $CaCO_3$ $NaHCO_3$
- molecular bases contain structures that react with H^+
  - ✓ mostly amine groups

Common Bases

Chemical Name	Formula	Common Name	Uses	Strength
sodium hydroxide	NaOH	lye, caustic soda	soap, plastic, petrol refining	Strong
potassium hydroxide	KOH	caustic potash	soap, cotton, electroplating	Strong
calcium hydroxide	$Ca(OH)_2$	slaked lime	cement	Strong
sodium bicarbonate	$NaHCO_3$	baking soda	cooking, antacid	Weak
magnesium hydroxide	$Mg(OH)_2$	milk of magnesia	antacid	Weak
ammonium hydroxide	NH_4OH, $\{NH_3(aq)\}$	ammonia water	detergent, fertilizer, explosives, fibers	Weak